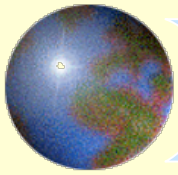
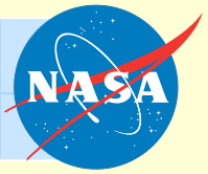


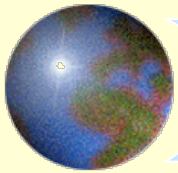


NASA Earth System Science at 20 Symposium

June 24, 2009

Michael J. Kurylo

Goddard Earth Sciences and Technology Center



Atmospheric Composition Research: Background and History

- *This is a story about the successful interface between scientific research and international environmental policy.*
- *NASA's unique role in this story stems from its ability to bring to the table a wealth of different tools from both the R&A and satellite communities.*
- *However, the setting for this story was developed well before the National Advisory Committee on Aeronautics (NACA) was transformed into NASA.*

The First Photochemical Theory for Ozone

Chapman

In 1929, **Sydney Chapman** introduces the first mechanism to describe the photochemistry of ozone in the atmosphere:

$$O_2 + UV \rightarrow O + O$$

$$O + O_2 + M \rightarrow O_3 + M$$

$$O_3 + UV \rightarrow O + O_2$$

$$O + O_3 \rightarrow 2\,O_2$$

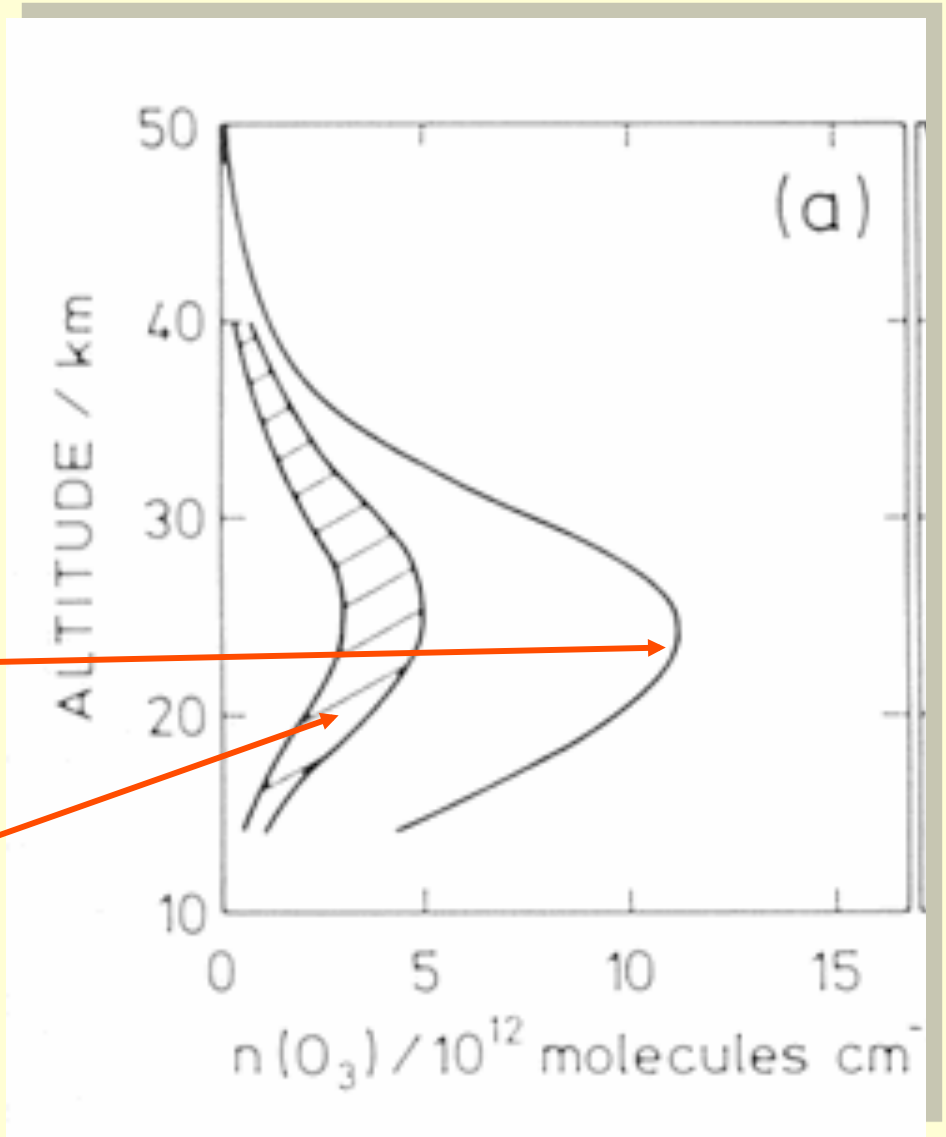
He highlights the role of atomic oxygen.

The Chapman Cycle: A Photochemical Puzzle

(1) $O_2 + h\nu \rightarrow O + O$
(2) $O + O_2 + M \rightarrow O_3 + M$
(3) $O_3 + h\nu \rightarrow O_2 + O$
(4) $O_3 + O \rightarrow O_2 + O_2$

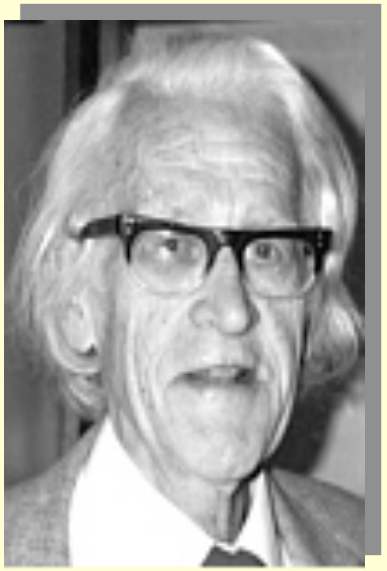
Theory

Observations



Ozone and Hydrogen

In 1950, Sir **David Bates** (Belfast) and Baron **Marcel Nicolet** (Brussels) suggest that hydrogen radicals (H, OH, HO_2) produced by photolysis of water vapor and methane provide a major ozone destruction mechanism in the ***mesosphere.***



Bates

In the mid-1960's **J. Hampson** in Canada suggests that similar processes can destroy ozone in the ***stratosphere.***

Nicolet

$OH + O_3 \rightarrow HO_2 + O_2$

$HO_2 + O \rightarrow OH + O_2$

Net: $O + O_3 \rightarrow 2O_2$

Ozone and Nitrogen

Crutzen

$NO + O_3 \rightarrow NO_2 + O_2$

$NO_2 + O \rightarrow NO + O_2$

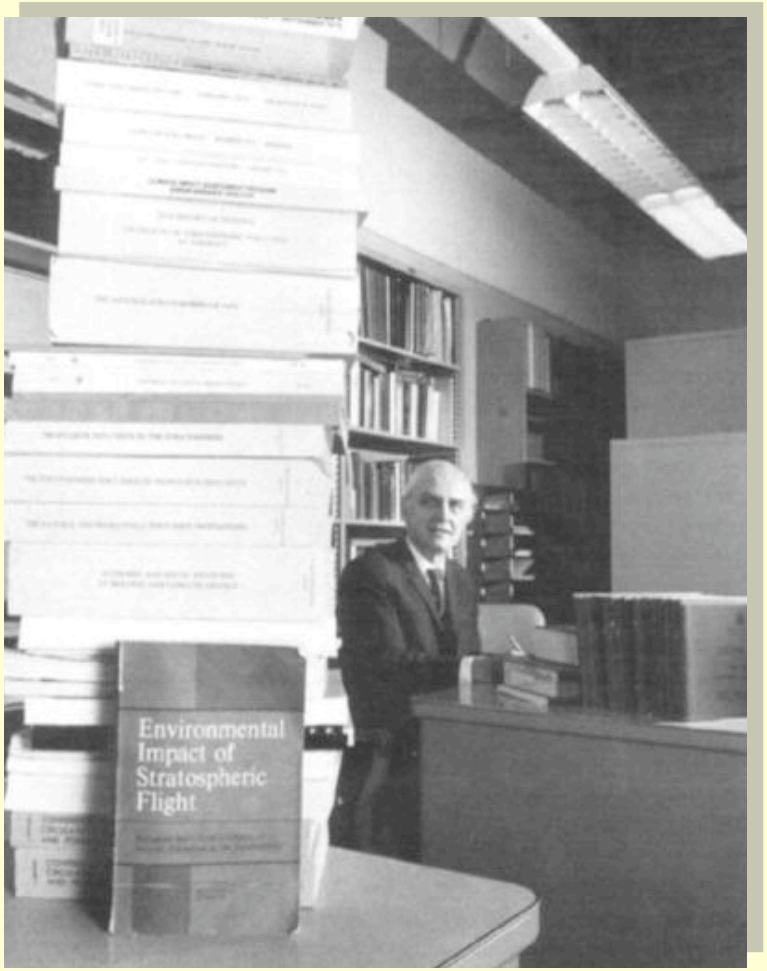
Net: $O + O_3 \rightarrow 2O_2$

Around 1970, **Paul Crutzen** shows that the major ozone loss in the stratosphere is provided by a catalytic cycle involving the presence of nitric oxide (NO).

Nitric oxide is produced in the stratosphere by oxidation of nitrous oxide (N_2O), a gas that is produced by bacteria in soils.

Nitrogen compounds in the stratosphere were first detected by **David Murcray** (U. of Denver) using a high altitude balloon-borne instrument.

The Possible Impact of Aviation



Johnston

In 1971, **Harold Johnston** (University of California at Berkeley) suggests that the nitrogen oxides released as engine exhaust from a projected fleet of **supersonic aircraft** could result in substantial ozone depletion.

An intensive research program, the **Climatic Impact Assessment Program** (CIAP) is initiated by the US Department of Transportation (1972-1974).

This initiated the **golden age** of stratospheric research.

Ozone and Chlorine

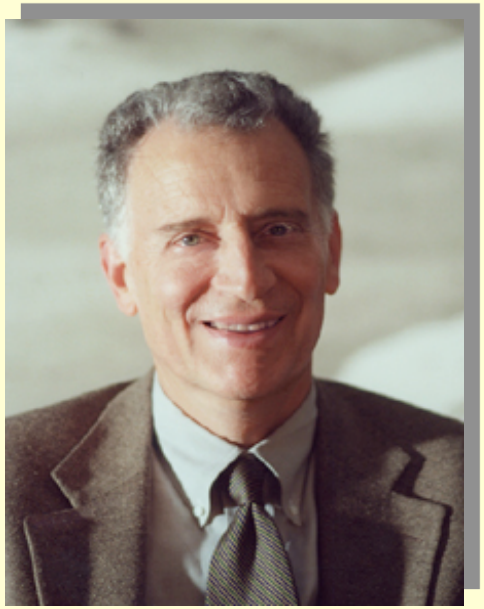
In 1974, **Richard Stolarski** and **Ralph Cicerone**, then at the University of Michigan, suggest that **chlorine** could also catalytically destroy ozone in the stratosphere. They had been studying, for NASA, the possible impacts of solid rocket propellants such as used by the **Space Shuttle**.

$$Cl + O_3 \rightarrow ClO + O_2$$

$$ClO + O \rightarrow Cl + O_2$$

Net: $O + O_3 \rightarrow 2O_2$

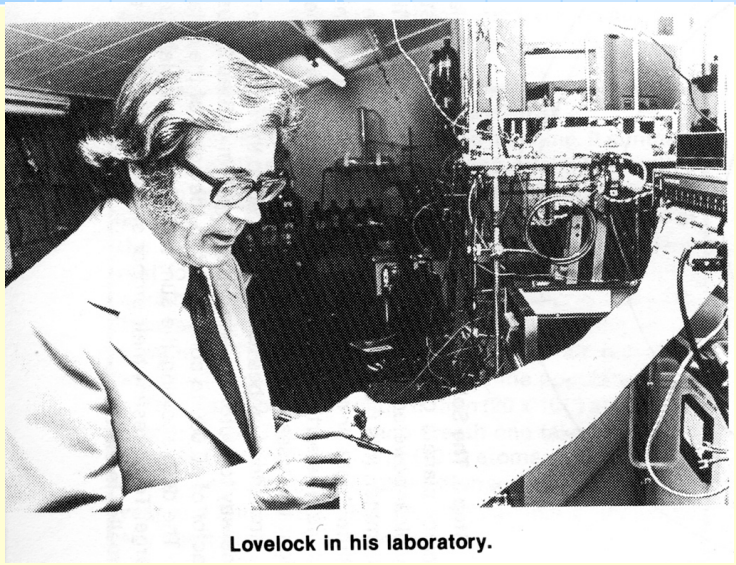
Stolarski



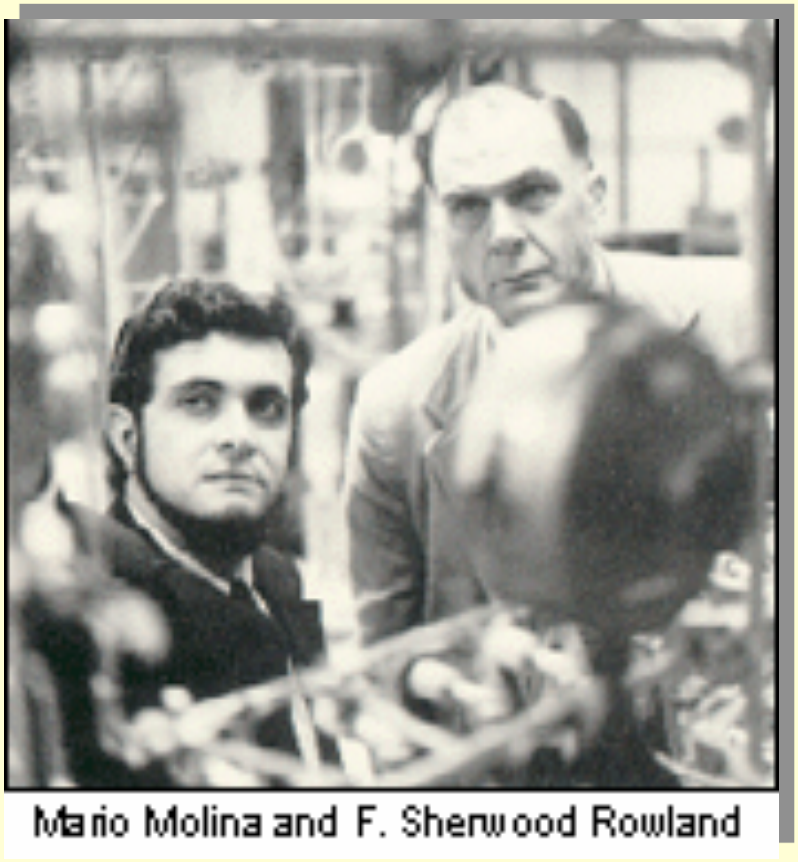
Cicerone

Chlorofluorocarbons and Ozone

In 1973, **James E. Lovelock** detects **chlorofluorocarbons** in the atmosphere.

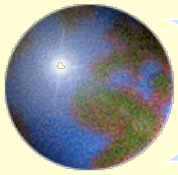


Lovelock in his laboratory.

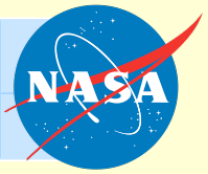


Mario Molina and F. Sherwood Rowland

In 1974, **Mario Molina** and **Sherry Rowland** at the University of California at Irvine show that these industrially manufactured chemicals provide the **major source of stratospheric chlorine** and pose a significant threat to the ozone layer.



The Birth of a Program



The concern over halogen-catalyzed destruction of ozone initiated international focus on stratospheric photochemistry and kinetics. In June 1975, the US Congress passed legislation directing NASA

"To conduct a comprehensive program of research, technology and monitoring of the phenomena of the upper atmosphere."

This language in NASA's FY1976 authorization bill, gave the Agency a clear mandate to perform research concerned with depletion of the ozone layer, and NASA's Upper Atmosphere Research Program was born.

Halley Bay, Antarctica Total Ozone: October Monthly Means

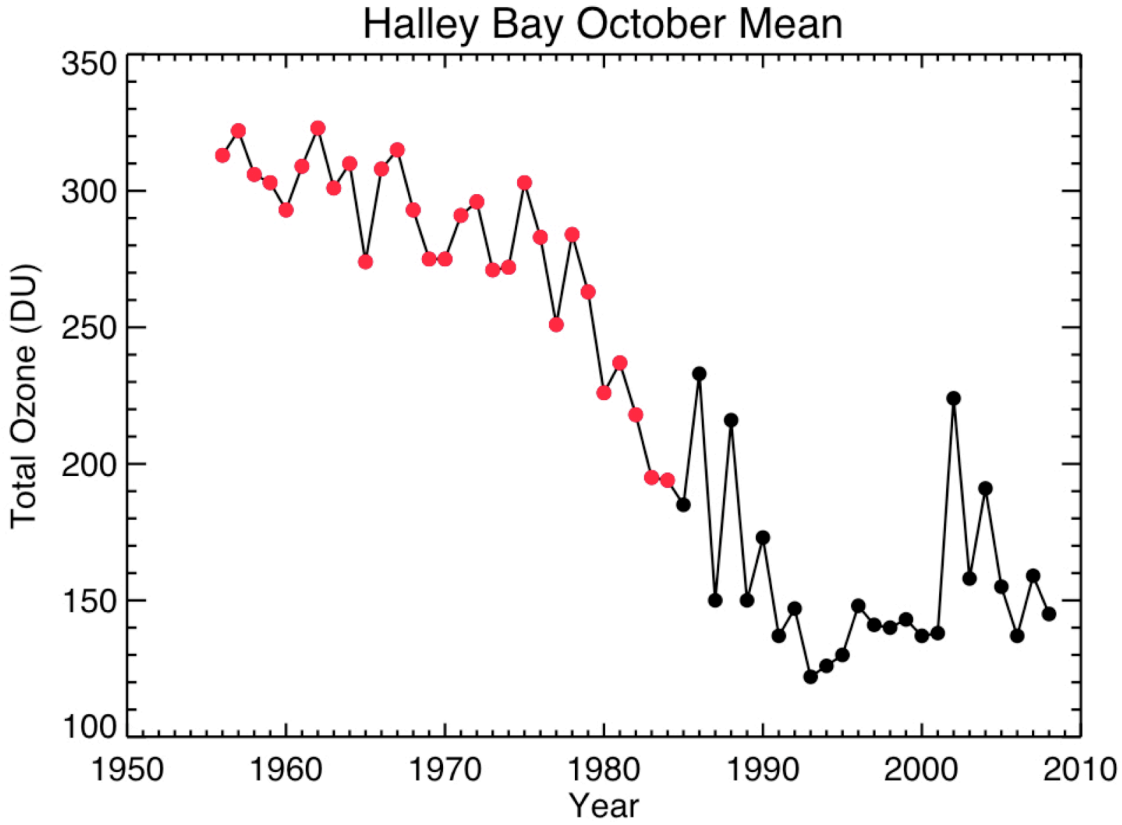


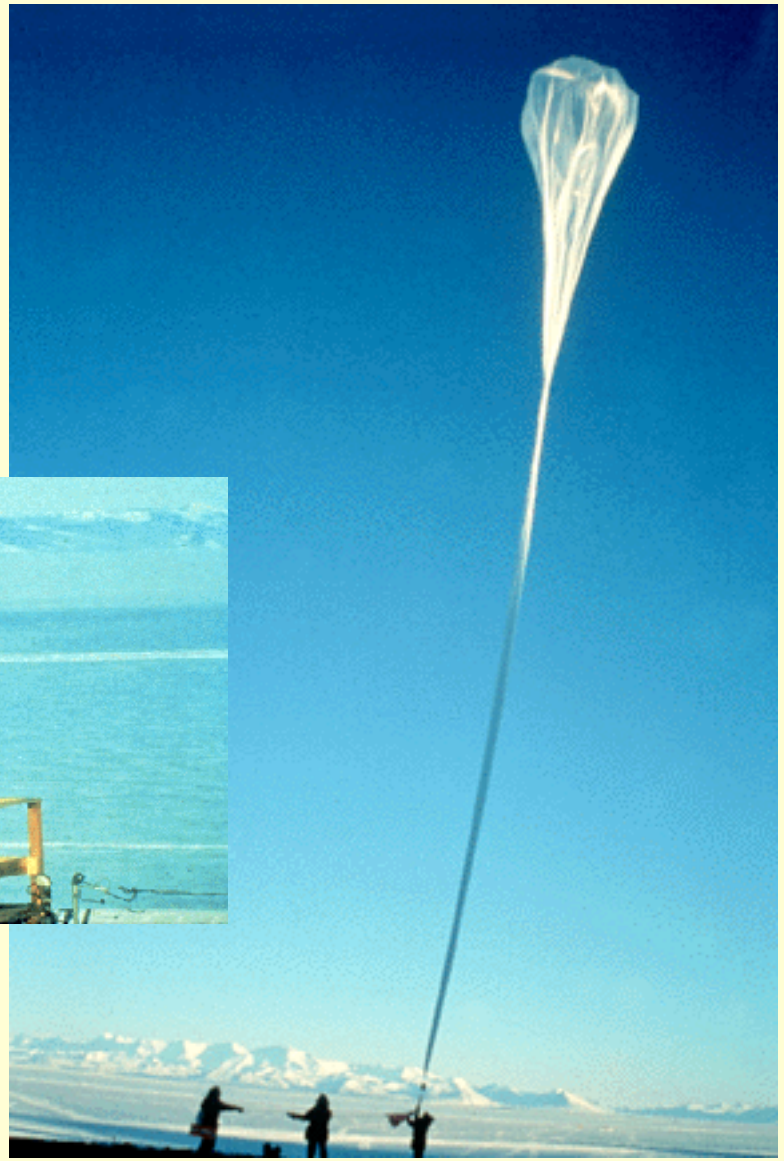
Figure 1. October mean total column ozone abundance from Dobson spectrometer measurements at Halley Bay, Antarctica (75.35°S, 26.34°W). Updated from Jones *et al.* [1995]. The data originally published by Farman *et al.* [1985] are shown in red. (Data courtesy of J. Shankin, British Antarctic Survey.)

Ozone Hole Hypotheses: Dynamics vs. Chemistry

- Dynamics: low ozone air lifted from the troposphere upward from 8-12 km into ozone hole region
  - Measure N_2O
- Nitrogen Chemistry: solar production of odd nitrogen (NOy). NOx catalytic cycle causes large ozone loss
  - Measure NO and Noy
- Heterogeneous chemistry: chlorine reservoir species are activated on the surfaces of polar stratospheric clouds producing a dramatic increase in active chlorine leading to chlorine catalytic ozone loss
  - Measure ClO

Ozone Hole History

1st National Ozone Expedition (NOZE-I) organized by NASA, NOAA and NSF arrives in Antarctica in August 1986.



Provides initial evidence that the ozone hole is related to chlorine chemistry.

Airborne Antarctic Ozone Experiment (AAOE 1987): A Defining Experiment

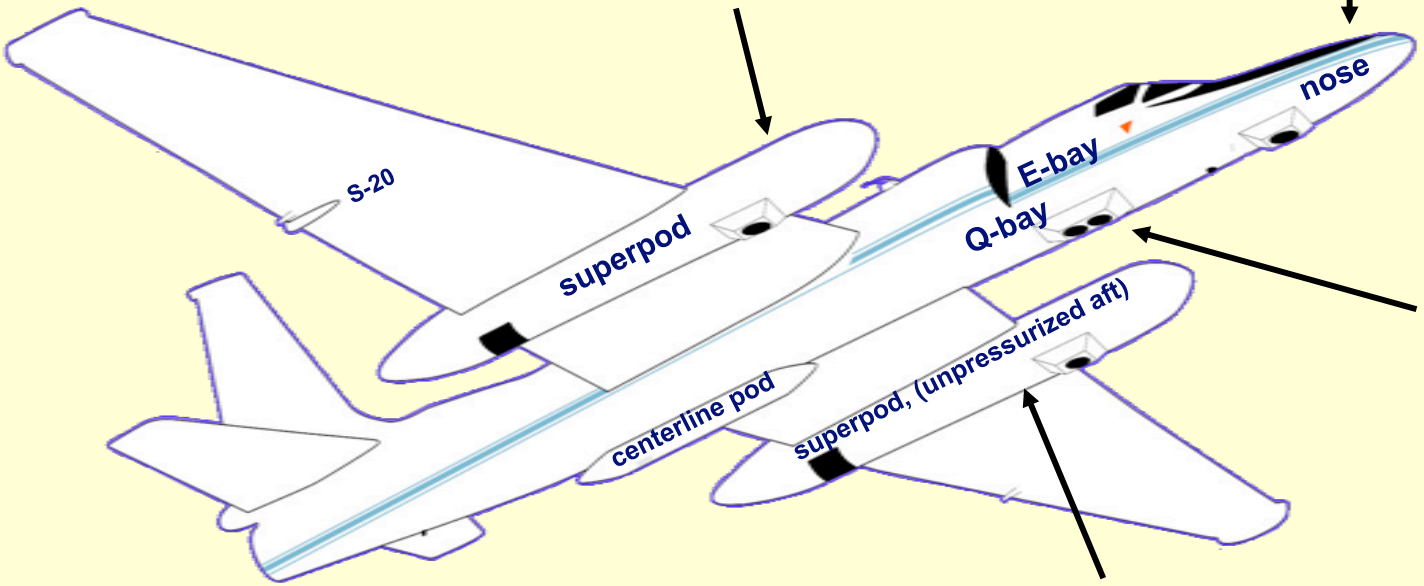
AAOE formulated in 1986 using instruments developed for the Stratospheric-Tropospheric Exchange Program (STEP).

Some instruments specifically built for the ER-2 aircraft (e.g., Harvard ClO-BrO).

AAOE 1987 (cont.)

Cloud particles
N_2O

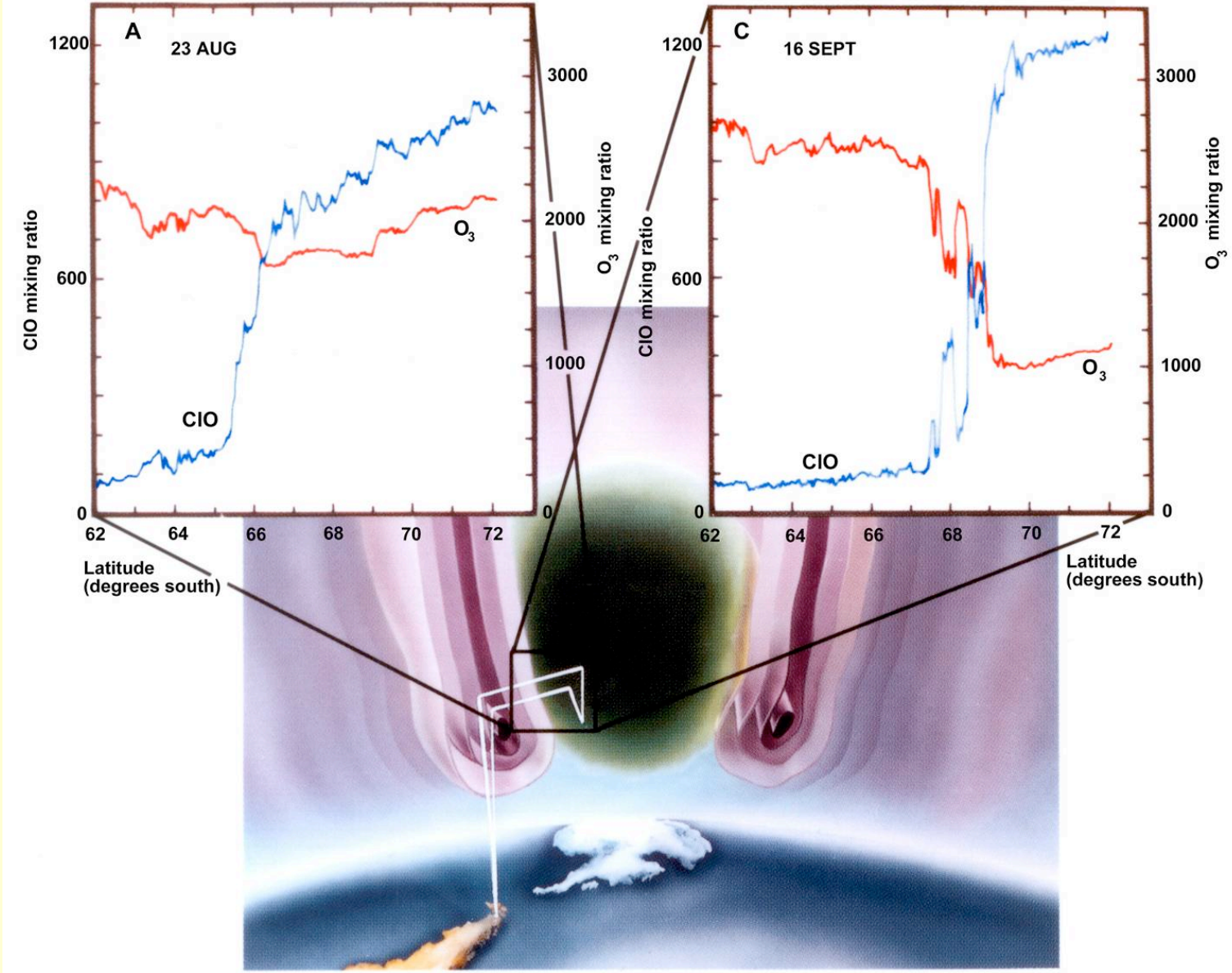
Winds, P, T
Gas can sample



H_2O
Ozone
NO, NOy

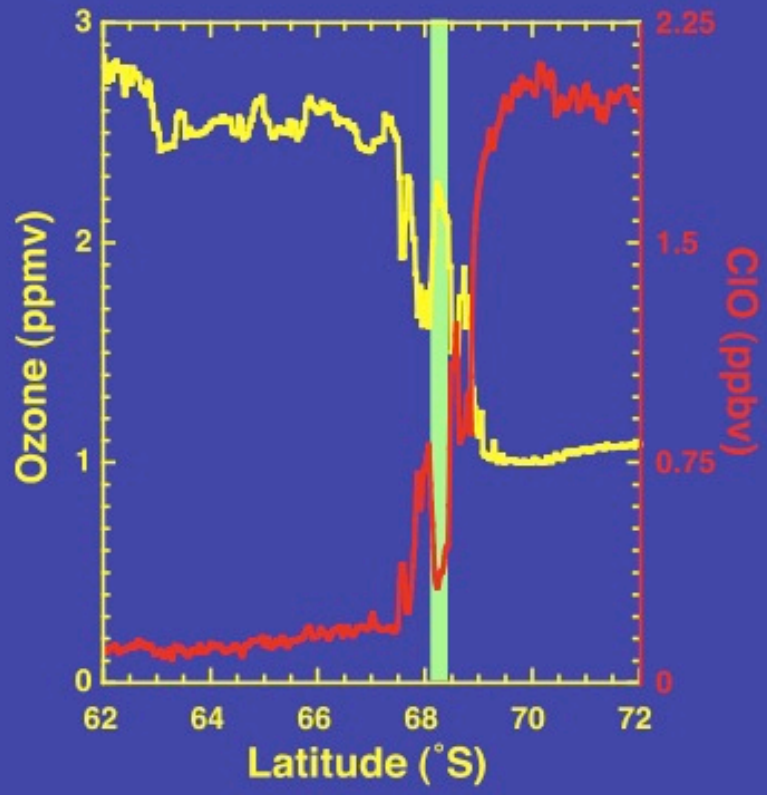
ClO, BrO
T-profile
Condensation nuclei

AAOE: 8/23/87 & 9/16/87 Data: The "Smoking Gun"



The Connection Between Chlorine Chemistry and the Antarctic Ozone Hole

AAOE: ClO & O_3 Observations



AAOE mission in August-September 1987: observations inside the polar vortex show high ClO is related to a strong decrease of ozone over the course of the Antarctic spring

A successful NASA / NOAA / NSF / CMA partnership

The Antarctic ozone hole was found to result from chlorine chemistry
More than 60 publications written by the end of 1989 from AAOE data

The Arctic Vortex: AASE I (1989)

Highly elevated ClO abundances discovered in the Arctic vortex.

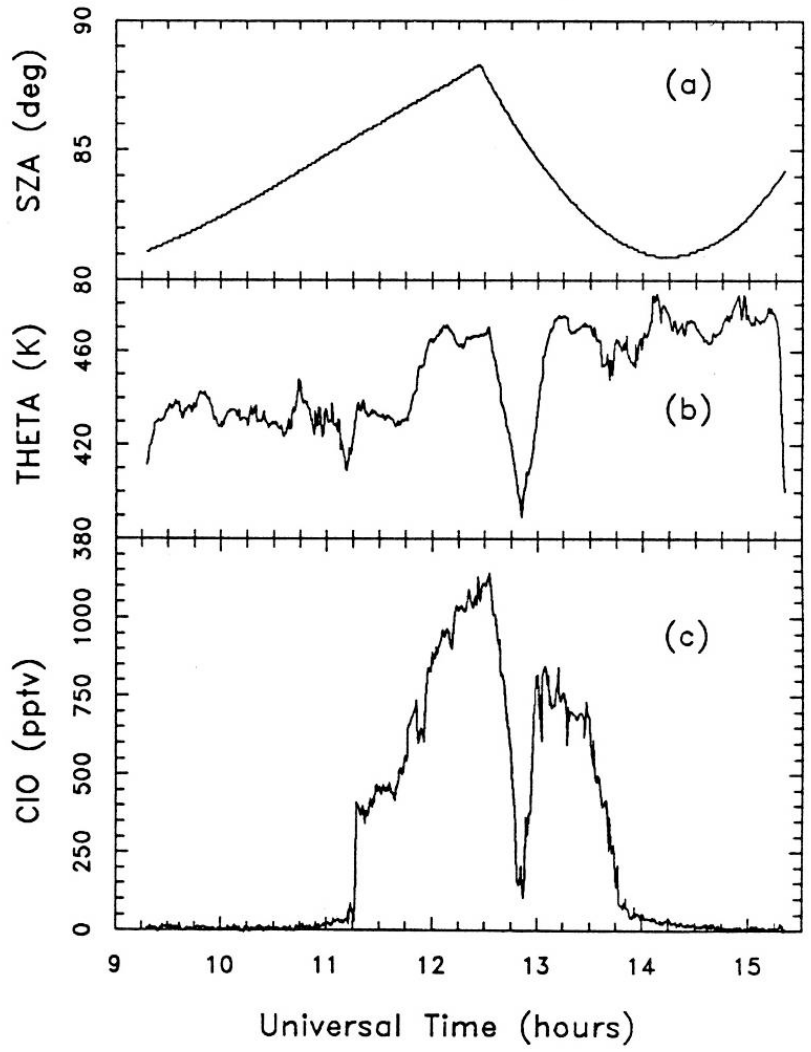


Fig. 3. Observed ClO mixing ratios plotted against Universal Time for February 10, 1989. Individual graphs are as in Figure 1.

Brune, et al. Geophysical Research Letters, Vol. 17, No. 4, p. 507.

AASE II: Very High ClO Over Northern US (January 1992)

US Senate votes 96-0 in February to accelerate the ban on CFC's.

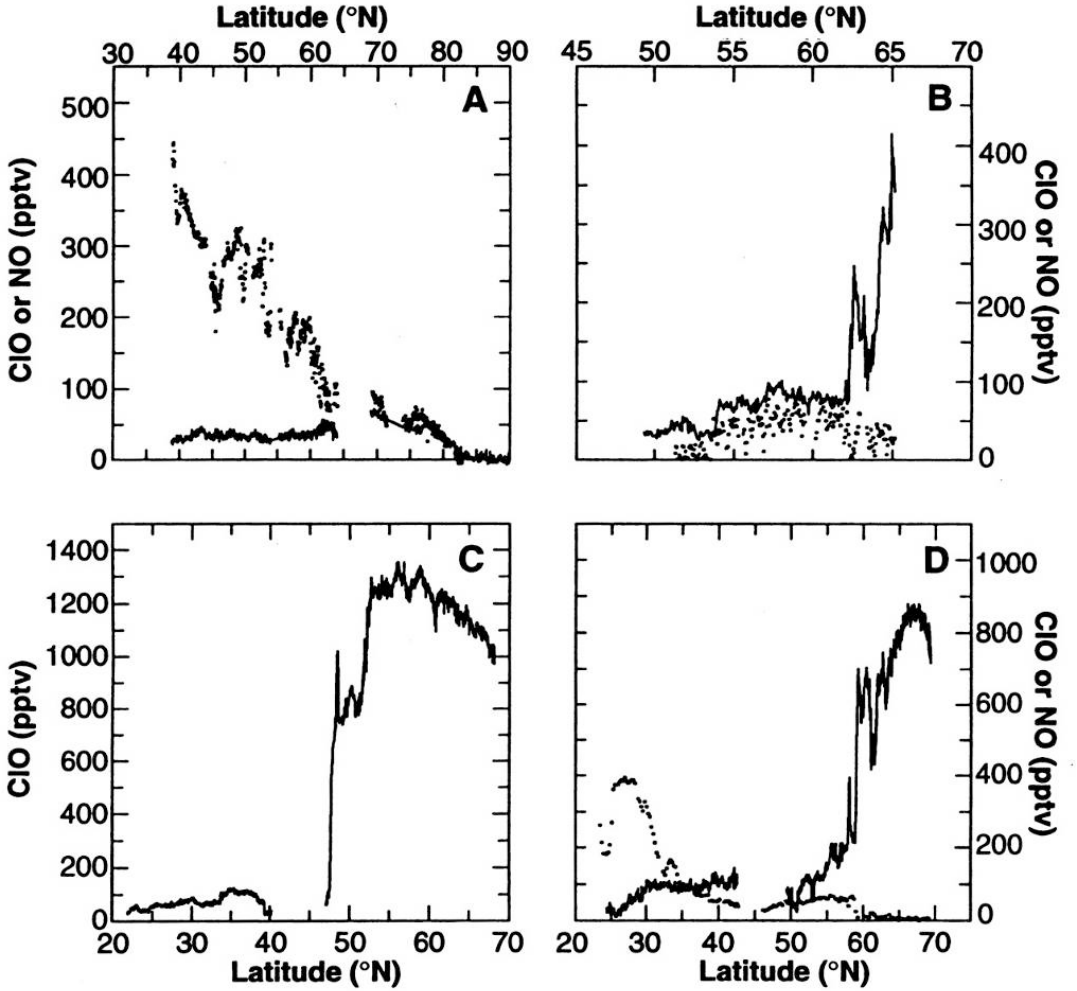


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Fig. 1. Mixing ratios of ClO and NO (in parts per trillion by volume) plotted versus latitude for selected flights of the NASA ER-2 aircraft during the AASE II mission: (**A**) 12 and 14 October 1991; (**B**) 12 December 1991; (**C**) 12 and 20 January 1992; (**D**) 13 and 22 February 1992. For each panel ClO data are represented as a solid line and NO data as discrete points.

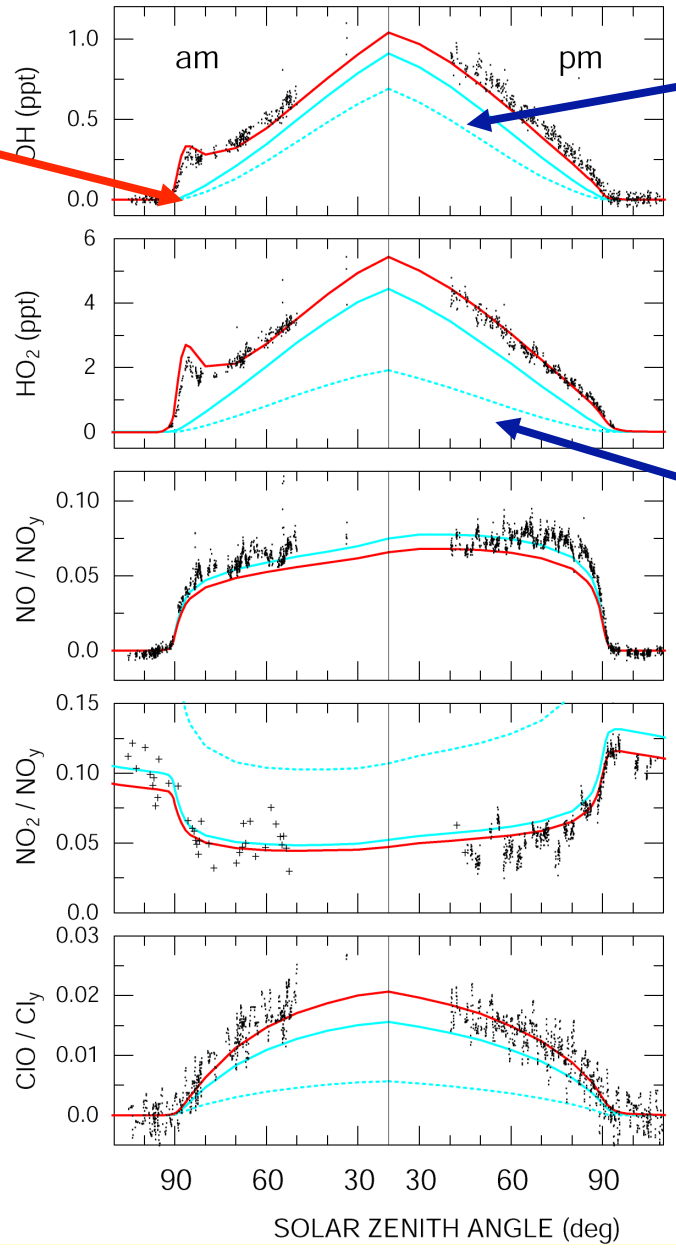
Airborne Arctic Stratospheric Expedition II
Fairbanks ALASKA
Stavanger NORWAY
Bangor MAINE
NASA · NOAA · CMA · NSF

First Joint Campaign with NASA's Atmospheric Effects of Aviation Project

JPL 1992: Gas Phase & Heterogeneous Chemistry Plus Updates Based on Recent (at the time) Lab Studies

JPL 1992: Gas Phase & Heterogeneous Chemistry

JPL 1992: Gas Phase Chemistry Only

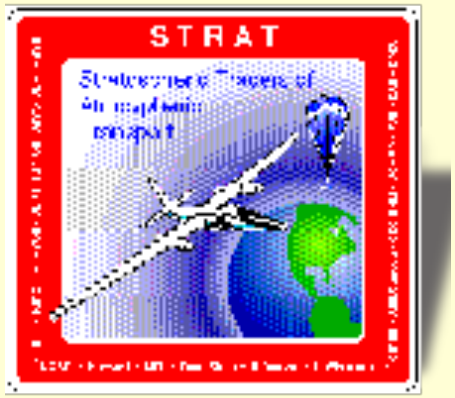


Stratospheric Photochemistry, Aerosols, and Dynamics Expedition: 1993

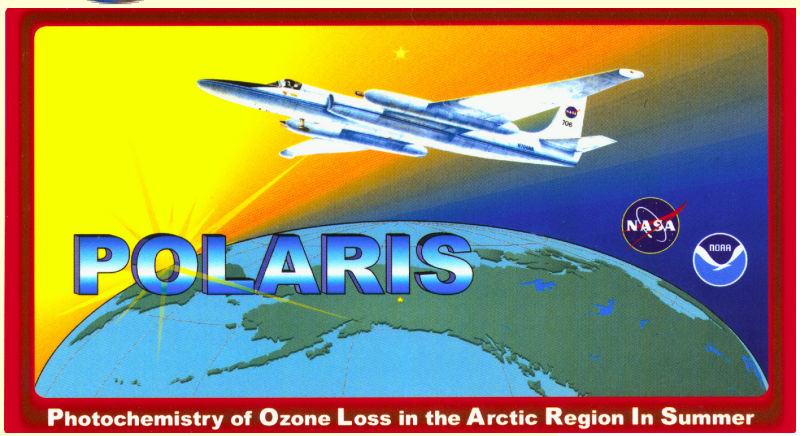
The Intensive Campaign Period of the Mid-1990's

Addressing a broad spectrum of science objectives:

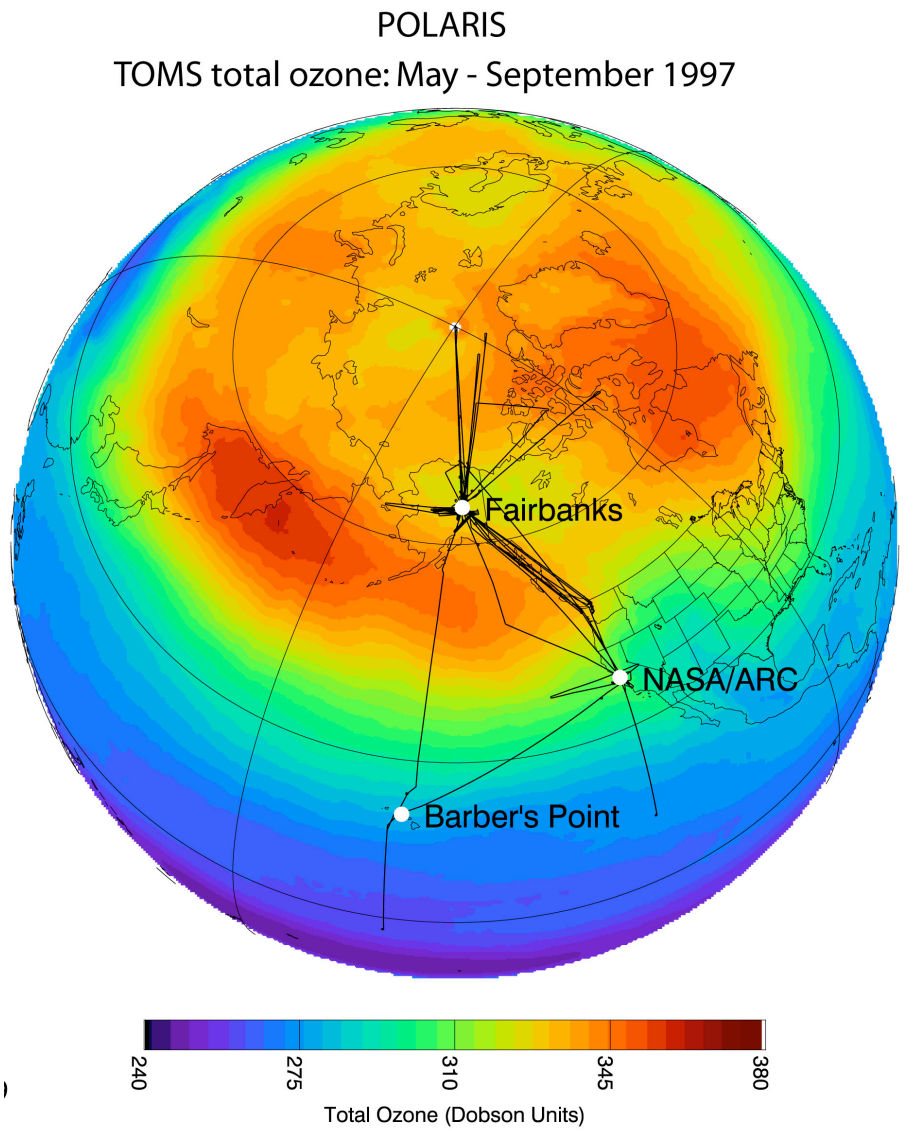
- ***Ozone depletion***
- ***Atmospheric effects of aviation***
- ***Global scale atmospheric transport of gases and particles***



POLARIS: NH Summer 1997



An aircraft campaign designed to understand the seasonal behavior of polar stratospheric ozone as it changes from very high concentrations in spring to very low concentrations in autumn - attributed to an increased role of NO_x catalytic cycles during periods of prolonged solar illumination as occur at high latitudes during summer

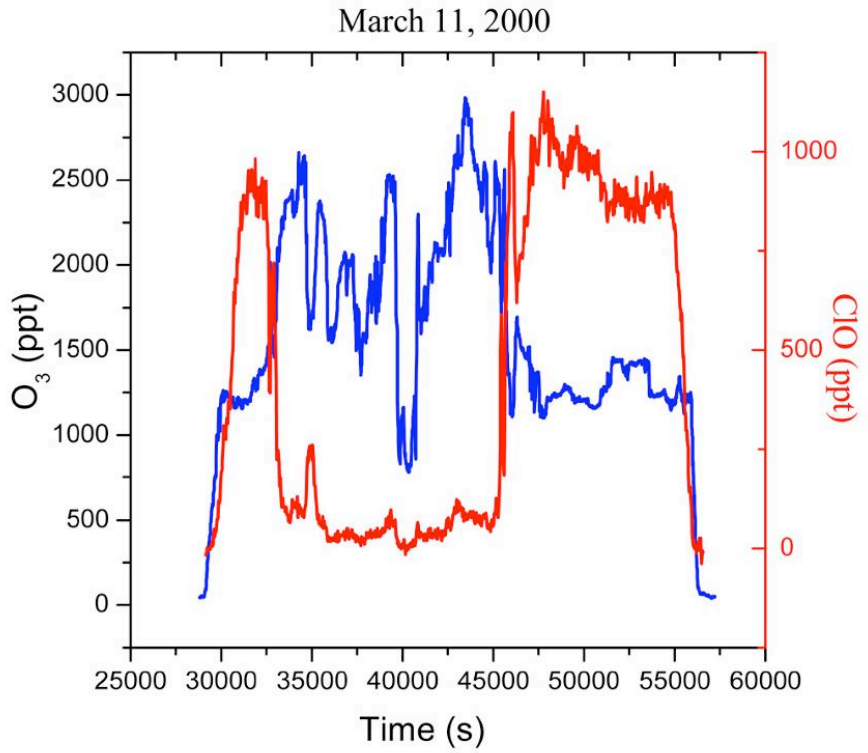


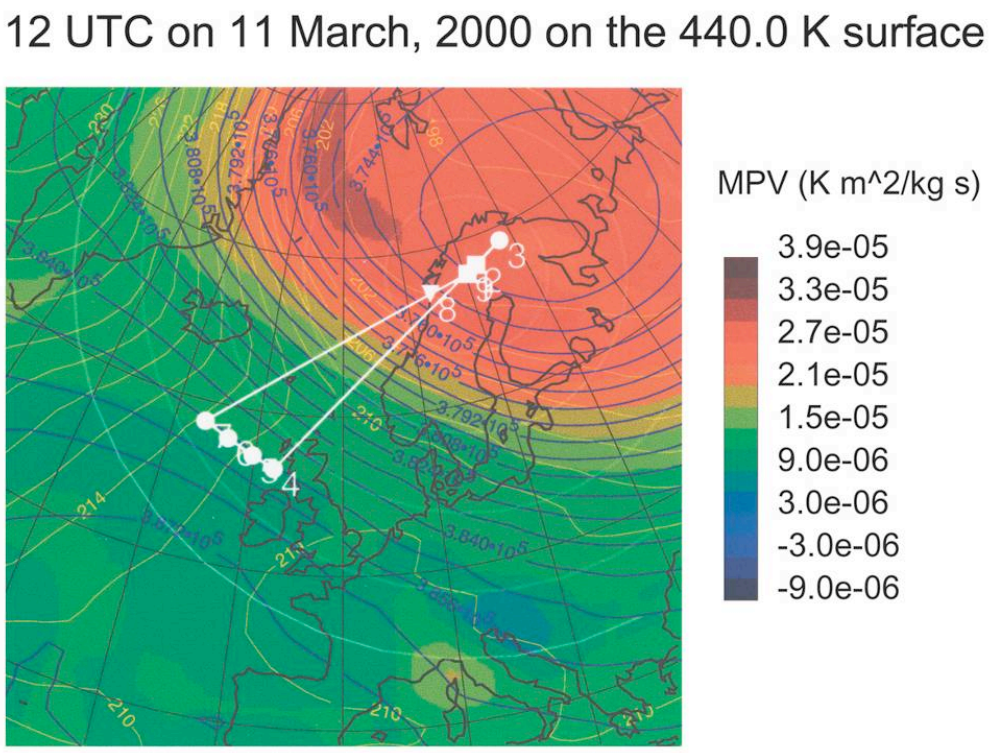
Return to the Arctic Vortex: 1999/2000 Winter

SAGE III Ozone Loss and Validation Experiment (SOLVE)
Third European Stratospheric Experiment on Ozone (THESEO)

SOLVE / THESEO (2000):

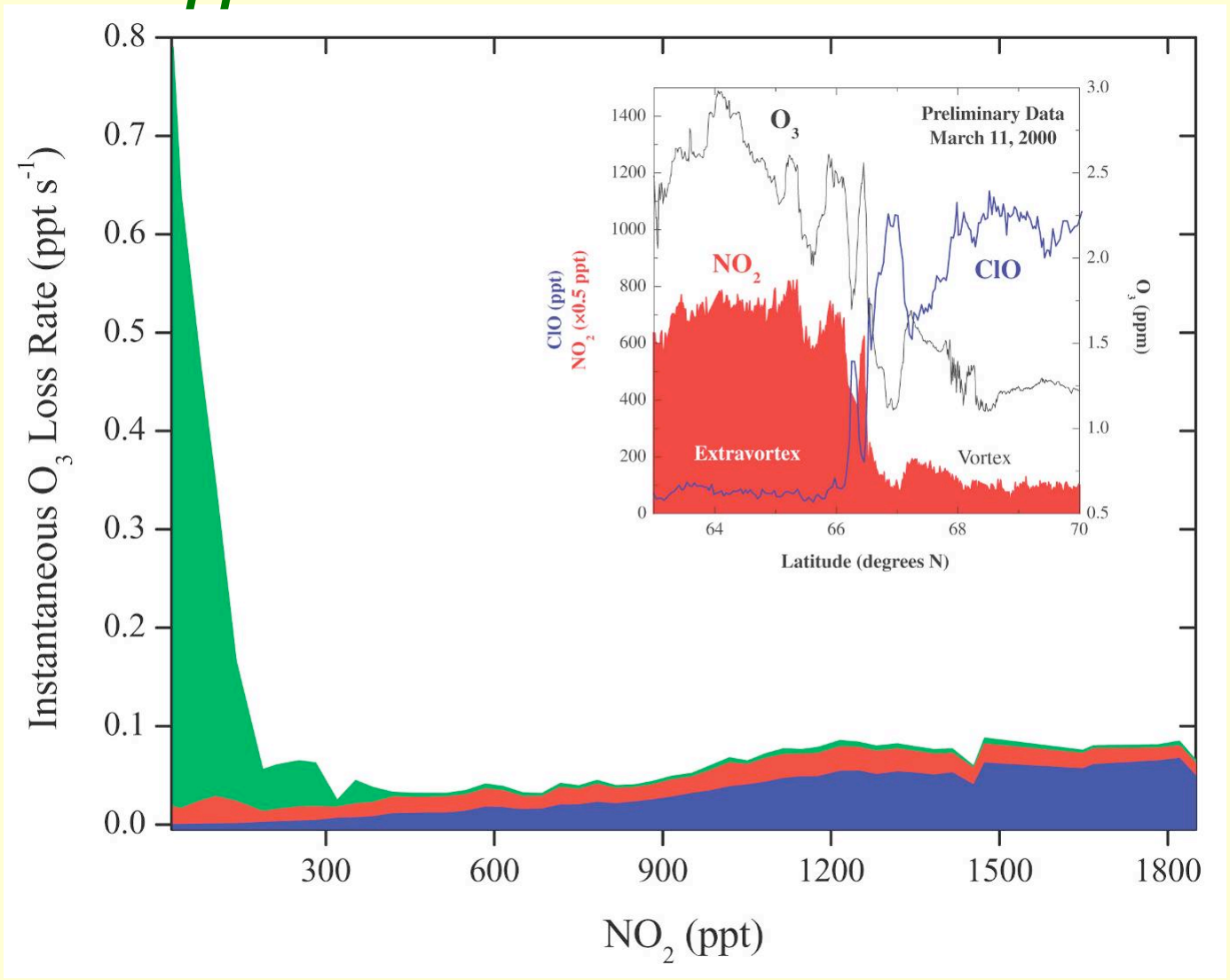
Dramatic Signature of ClO/O_3 Anti-correlation

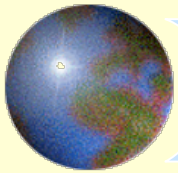




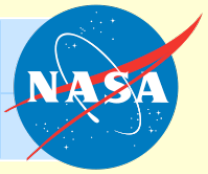
SOLVE / THESEO Results

Loss Rates of Ozone as a Function of NO_2 Mapped Out from Direct Observations





SOLVE / THESEO (1999/2000)

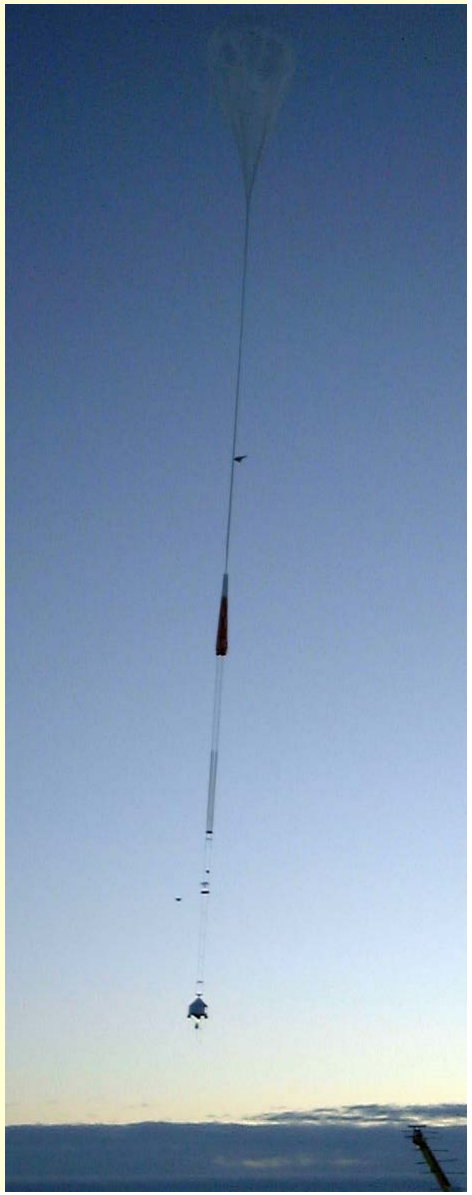


An outstanding scientific success and demonstration of international cooperation

- O_3 loss by rate-limiting radicals determined up to 90°N
  - budget inconsistencies remain
- Large “ice particle” discovery has far reaching consequences for understanding atmospheric microphysics and polar ozone changes
  - unknown nucleation process
  - non-equilibrium growth conditions
- Severe and extensive denitrification a known possibility in the future Arctic stratosphere
  - climate change effects
- Denitrification enhances ozone loss in inter-comparable stratospheric air parcels
  - significant effect dependent on seasonal conditions

SOLVE / THESEO (1999/2000)

Balloon Component



International Cooperation in Arctic Ozone Research (cont.)

Joint SOLVE-II / VINTERSOL-EUPLEX Campaigns (2003)

Second SAGE-III Ozone Loss and Validation Experiment (SOLVE-II)

Sites:

- DC-8: Kiruna, Sweden (Jan. 8-Feb. 6, 2003): Remote and In-situ payload
- Mk-IV + free flyer aerosol & H_2O balloons: Esrange, Sweden (flights in Nov. and March)

Goals:

- Validation of SAGE-III satellite observations
- Correlative measurements with ADEOS-II and ENVISAT and support for EC Vintersol campaign
- Diagnosis of ozone loss in January 2003
- Investigation of polar stratospheric clouds in mid-winter, particularly large nirtric-acid trihydrate particles

2007 Aircraft Campaign in Costa Rica

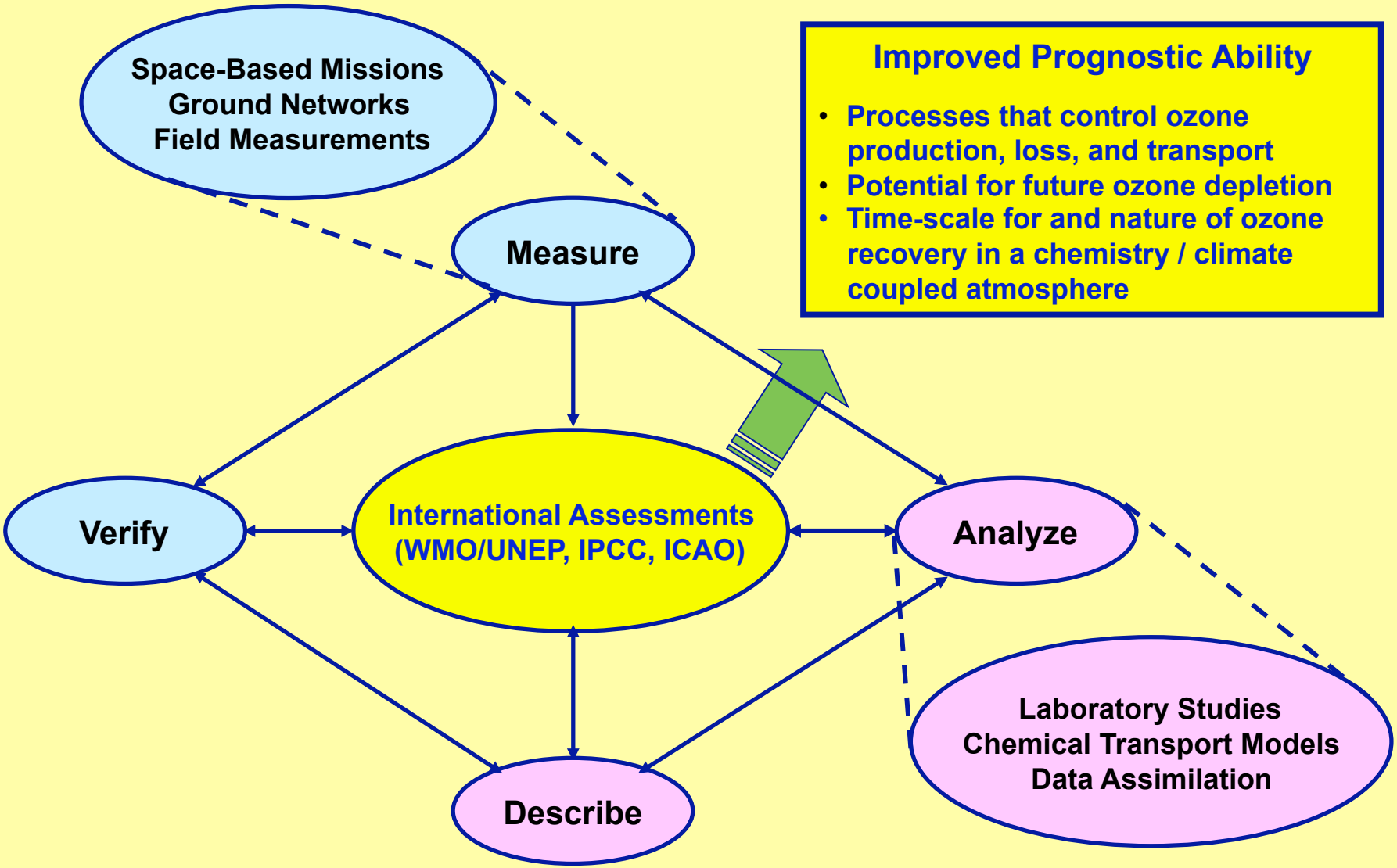
TC^4: Tropical Composition Cloud and Climate Coupling

NASA's TC^4 mission studied the Intertropical Convergence Zone in Central America, focusing on critical climatic processes: *clouds, dehydration, and chemical inputs to the stratosphere.*

The ER-2 obtained high-resolution remote sensing data; the WB-57F collected data in the critical tropopause region; and the DC-8 provided particle and chemical profiles in the upper troposphere.

Aircraft data validated A-Train satellite measurements and obtained key complementary information to decipher the basic processes.

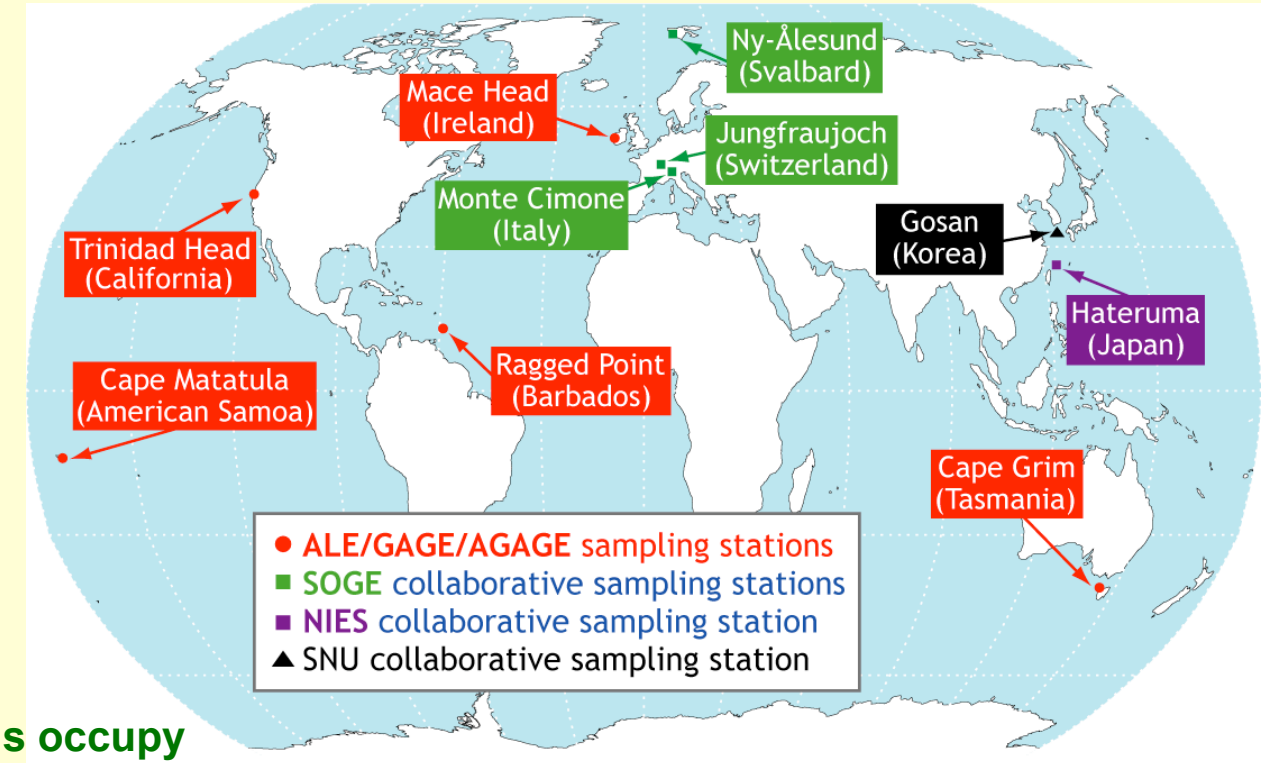
Interactive Research Elements: Addressing Ozone Depletion and Recovery



Advanced Global Atmospheric Gases Experiment and Affiliated Networks

The AGAGE, and its predecessors (the Atmospheric Lifetime Experiment, ALE, and the Global Atmospheric Gases Experiment, GAGE) have been measuring the composition of the global atmosphere continuously since 1978.

AGAGE is distinguished by its capability to measure over the globe at high frequency almost all of the important species in the Montreal Protocol to protect the ozone layer and almost all of the significant non-CO_2 gases in the Kyoto Protocol to mitigate climate change.

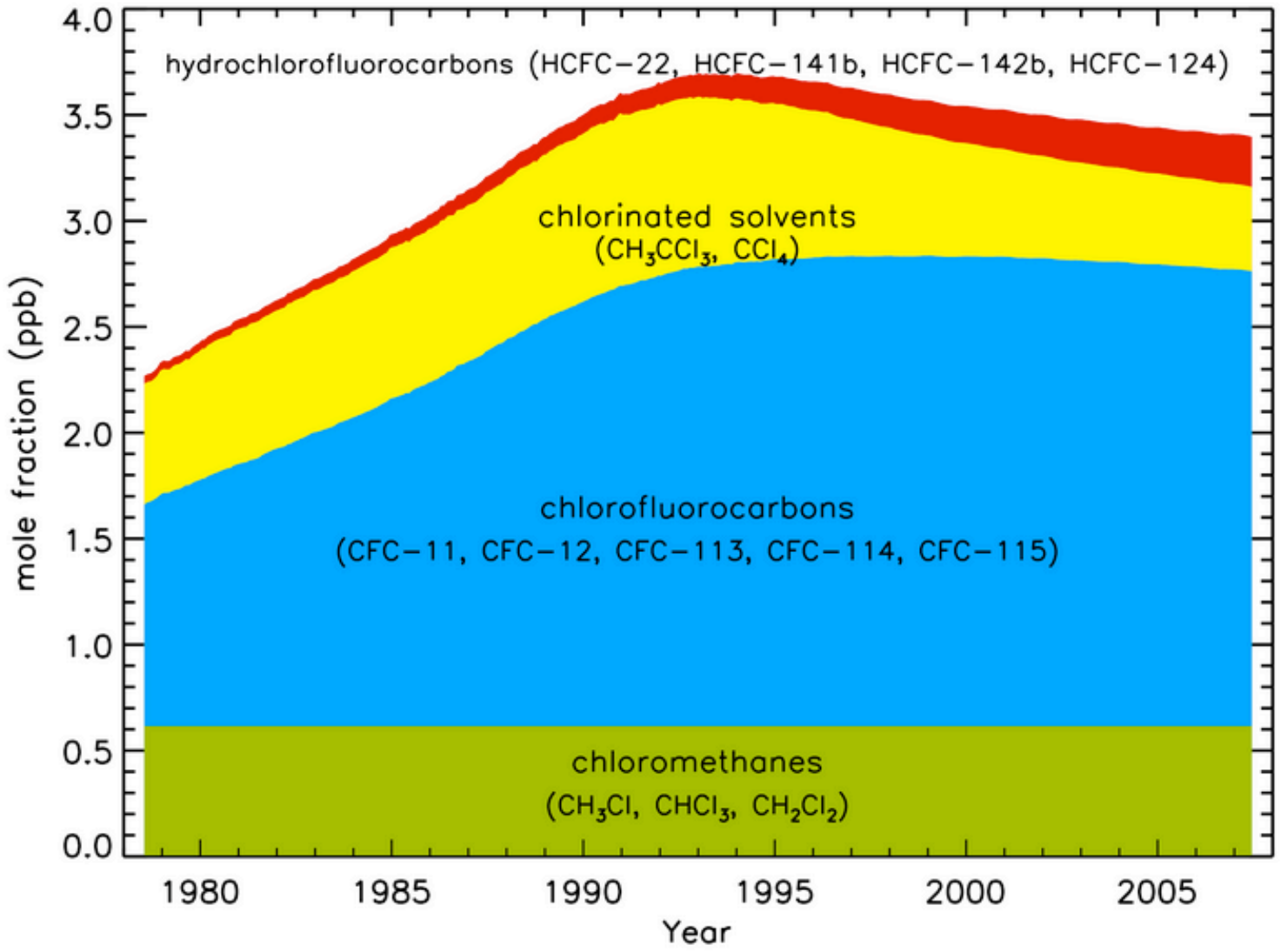


The ALE/GAGE/AGAGE stations occupy coastal & mountain sites around the world chosen to provide accurate measurements of trace gases whose lifetimes are long compared to global atmospheric circulation times.

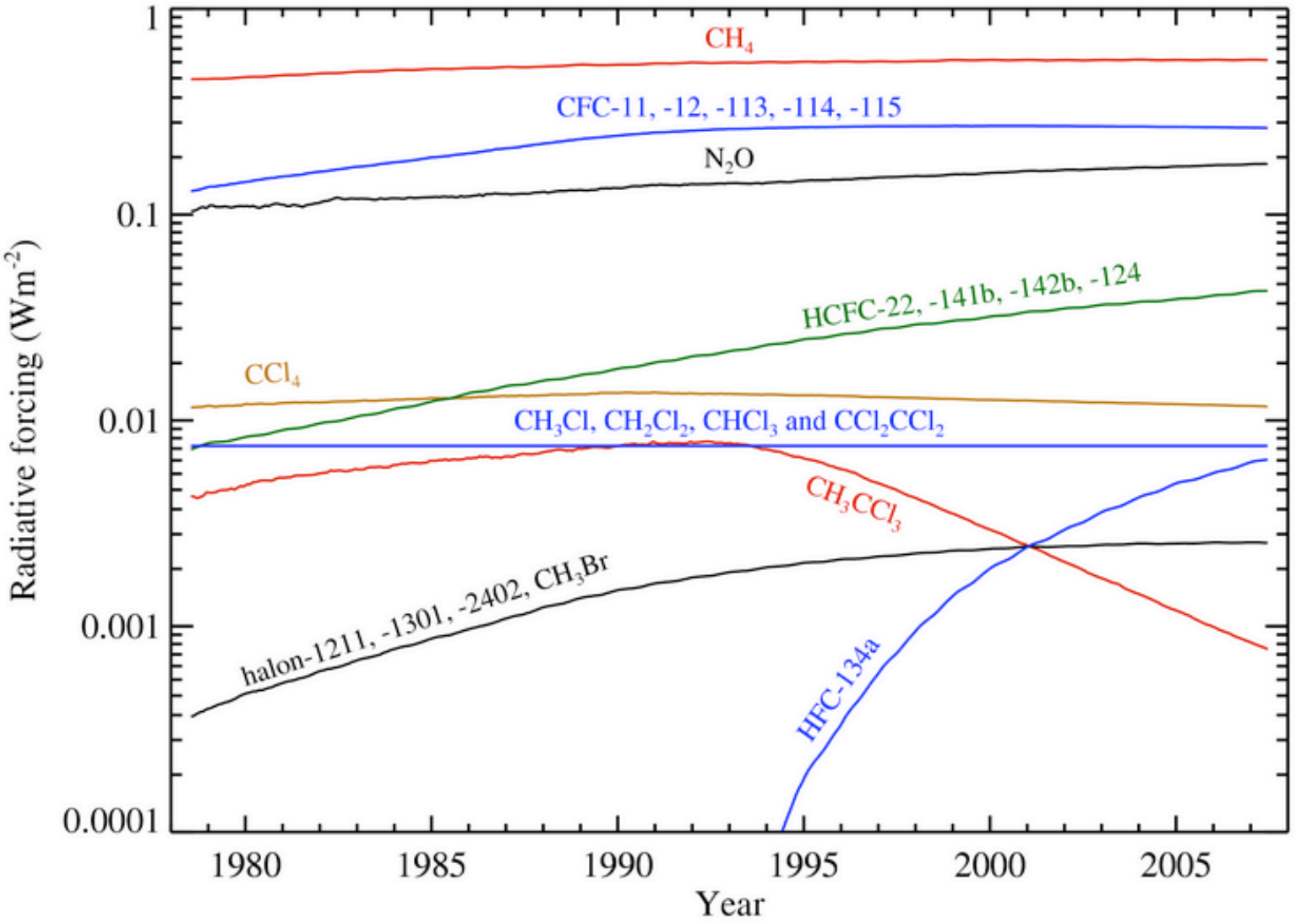
SOGE: System for Observation of Halogenated Greenhouse Gases in Europe
NIES: National Institute for Environmental Studies, Japan
SNU: Seoul National University, Korea.

AGAGE WEB SITE at http://agage.eas.gatech.edu

Tropospheric Organic Chlorine



Radiative Forcing from AGAGE Species



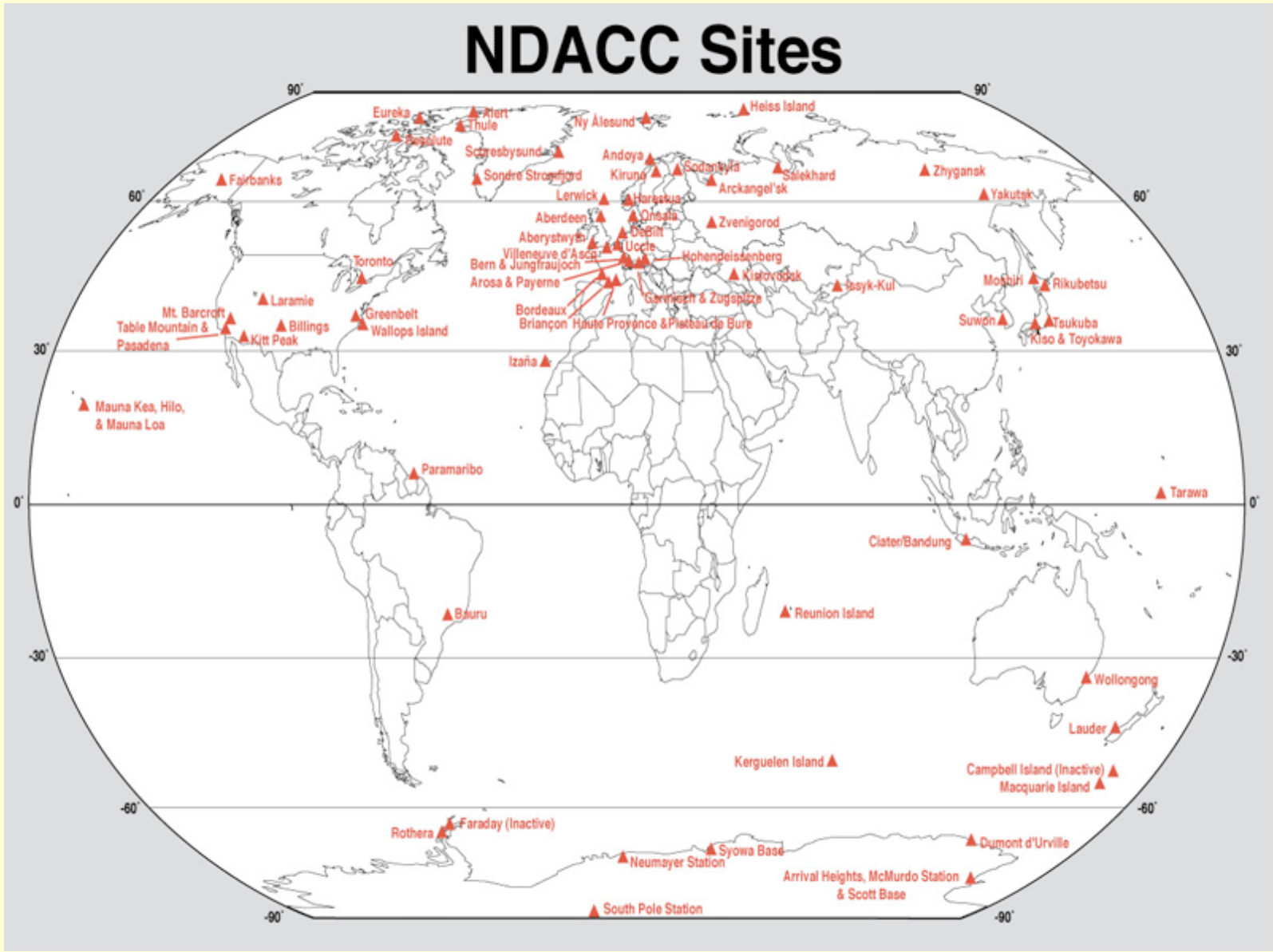
Network for the Detection of Atmospheric Composition Change

Exploring the Interface Between Changing Atmospheric Composition and Climate

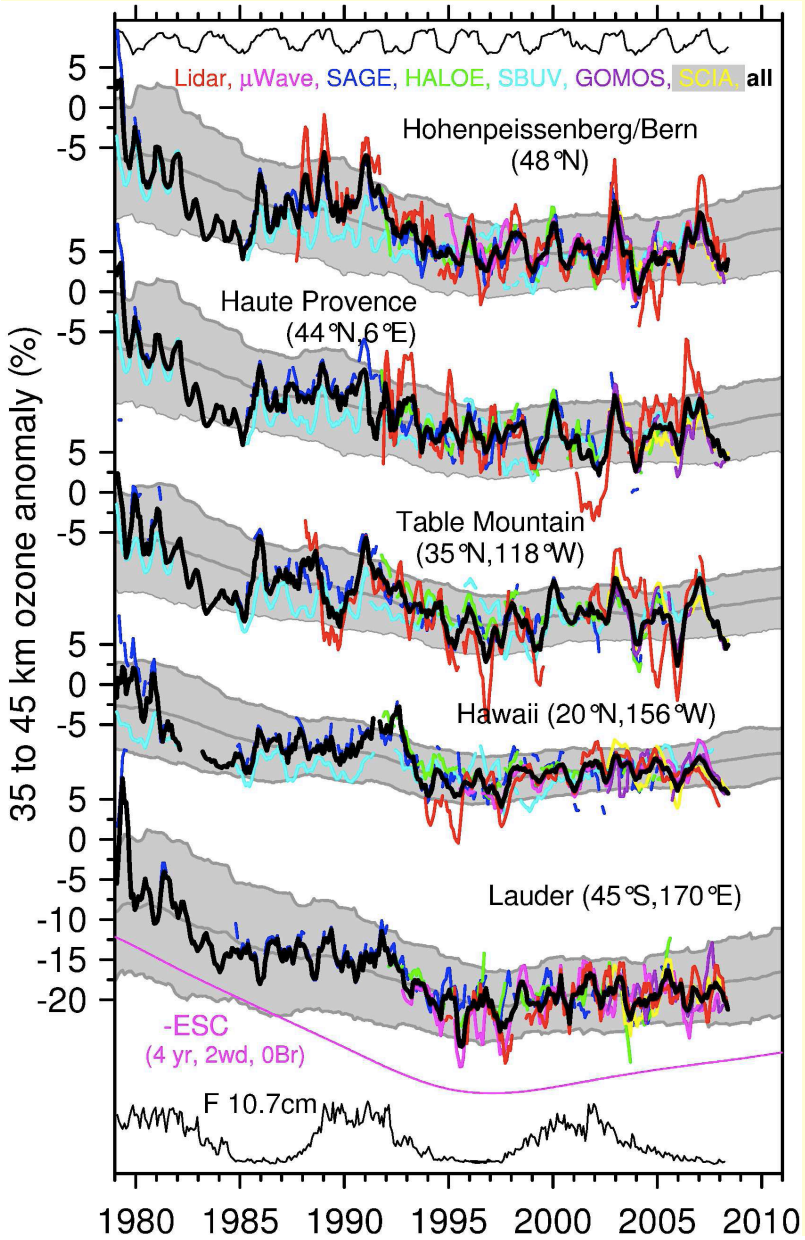
A set of more than 70 high-quality, remote-sensing research stations/sites for:

- ***studying the temporal and spatial variability of atmospheric composition and structure***
- ***detecting trends in overall atmospheric composition and understanding their impacts on the stratosphere and troposphere,***
- ***establishing links between climate change and atmospheric composition,***
- ***calibrating and validating space-based measurements of the atmosphere,***
- ***supporting process-focused scientific field campaigns, and***
- ***testing and improving theoretical models of the atmosphere.***

Network for the Detection of Atmospheric Composition Change



Ozone Anomalies from NDACC Stations Compared with Satellite Measurements

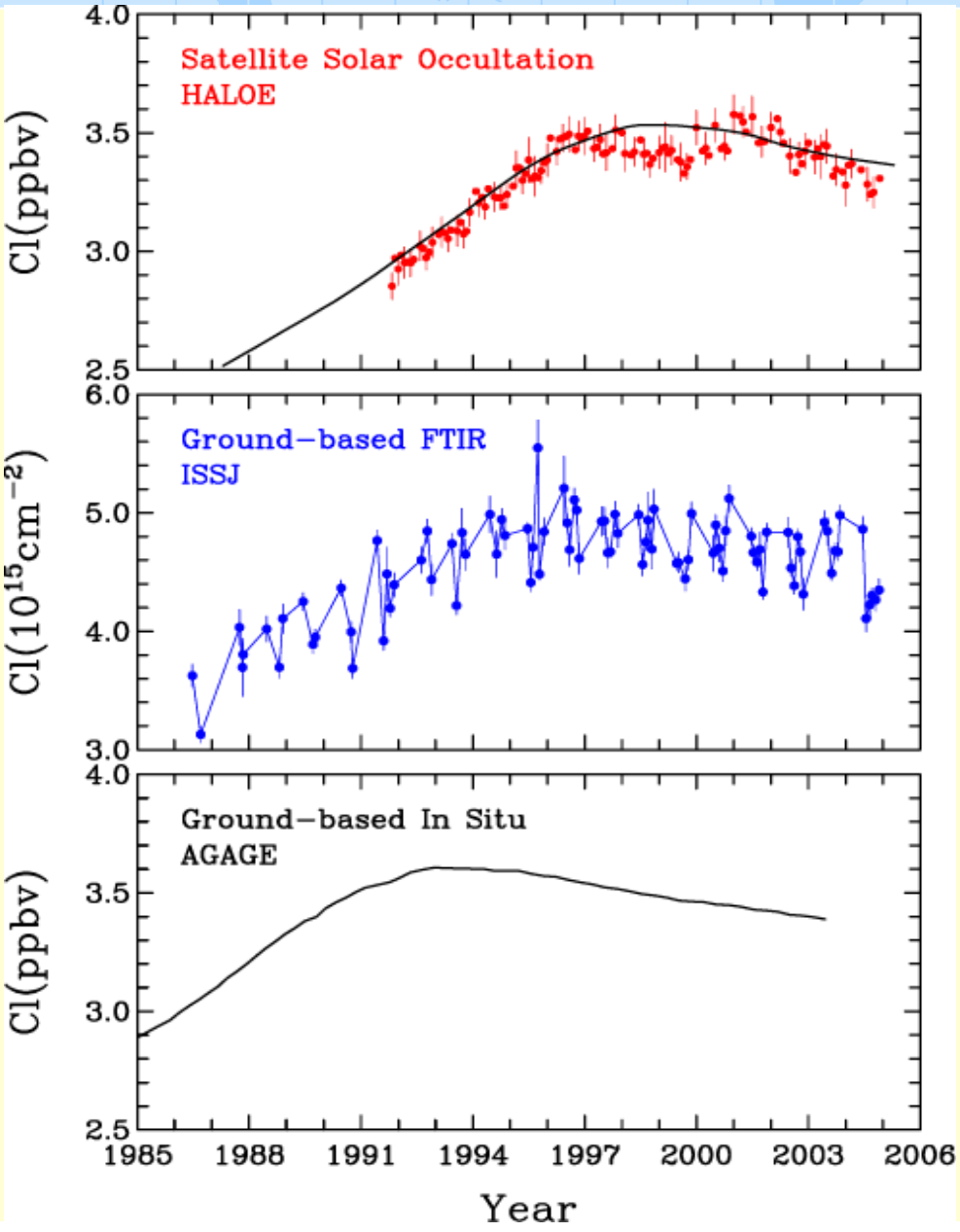


Anomalies are averaged over the 35 to 45 km range.

- **Black Line: Average of all available instruments.**
- **Grey underlay: CCMVal model simulations, 24 month running average 2 standard deviations.**
- **Observed data are smoothed by a five month running mean. Lidar and microwave data are station means; all other data are zonal means.**
- **The thin black lines at the top and bottom show negative 10 hPa zonal wind at the Equator as a proxy for the QBO, and 10.7 cm solar flux as a proxy for the 11-year solar cycle, respectively.**
- **The thin magenta line near the bottom shows inverted Effective Stratospheric Chlorine as a proxy for ozone destruction by chlorine (ESC, 4 years mean age, 2 years spectral width, no bromine, see Newman et al., 2006).**

Streinbrecht et al., Int, J. Remote Sensing, 2008

Cl Time Series for 55 km, Column and Surface



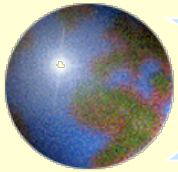
Satellite Measurements:
HALOE derived Cl. The solid black line is the UNEP baseline scenario lagged 5.3 years.

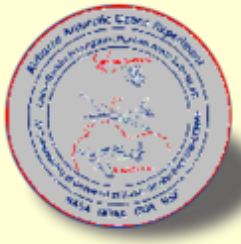
Ground-based Remote Sensing:
Jungfraujoch Station Cl derived from the summation of column HCl, $ClONO_2$, and modeled background ClO.

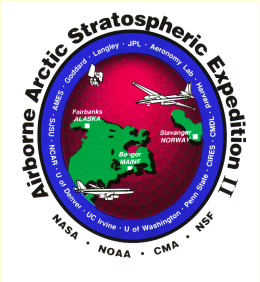
Ground-based In Situ:
AGAGE data

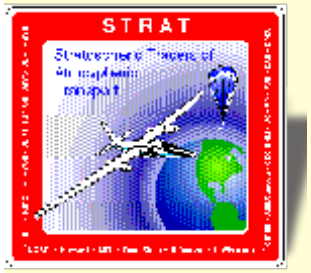
Russell and Anderson, 2005)

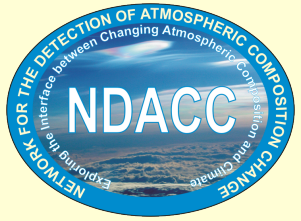
An Integrated Observations and Research Strategy











NASA's Involvement in Ozone Research

- *Space-based O_3 observations developed in the 1960's*
- *In early 1970's, rockets and high altitude aircraft exhaust hypothesized as major O_3 depleters*
- *Subsequently CFCs hypothesized as major O_3 depleter*
- *1976 NASA Authorization Act charters the development and maintenance of a comprehensive upper atmosphere research program*
- *1977 Clean Air Act Amendment mandates periodic reports on ozone and atmospheric halogen to Congress and EPA*
- *NASA provides key input to international ozone depletion assessments.*

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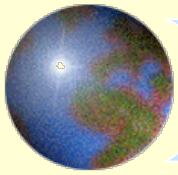
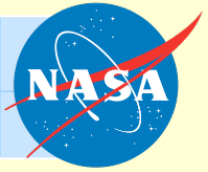


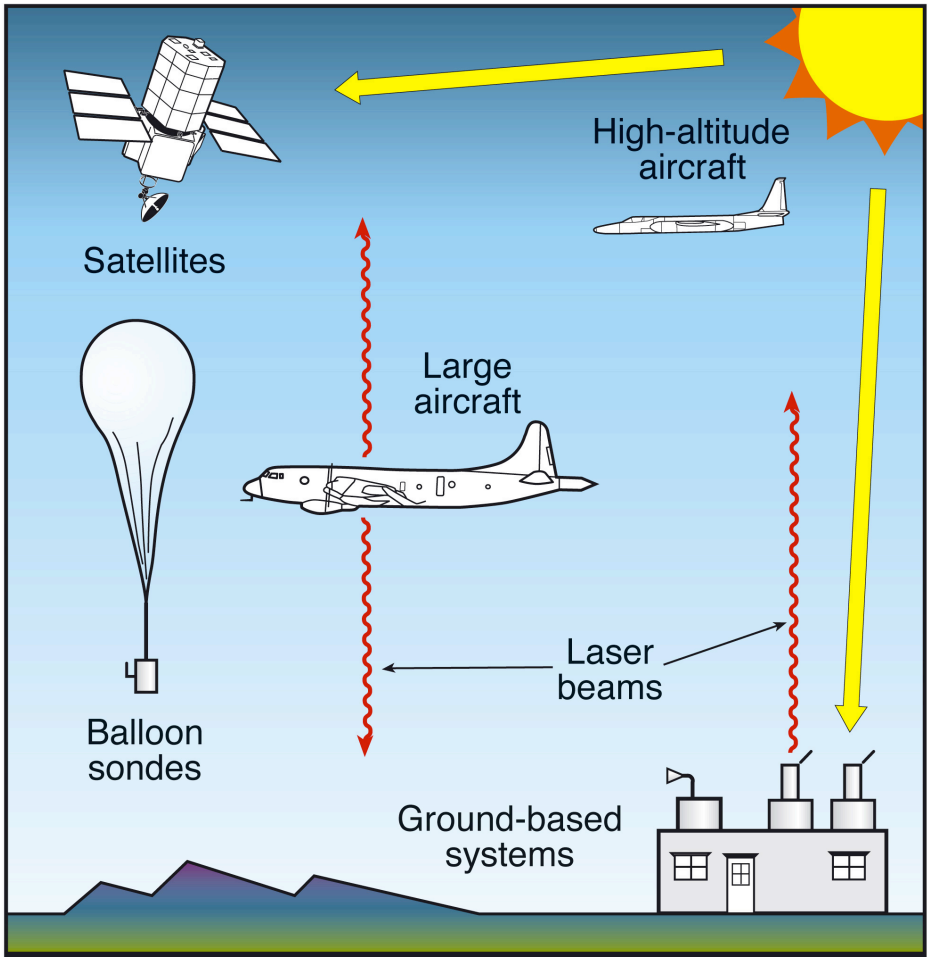
Back-Up Slides



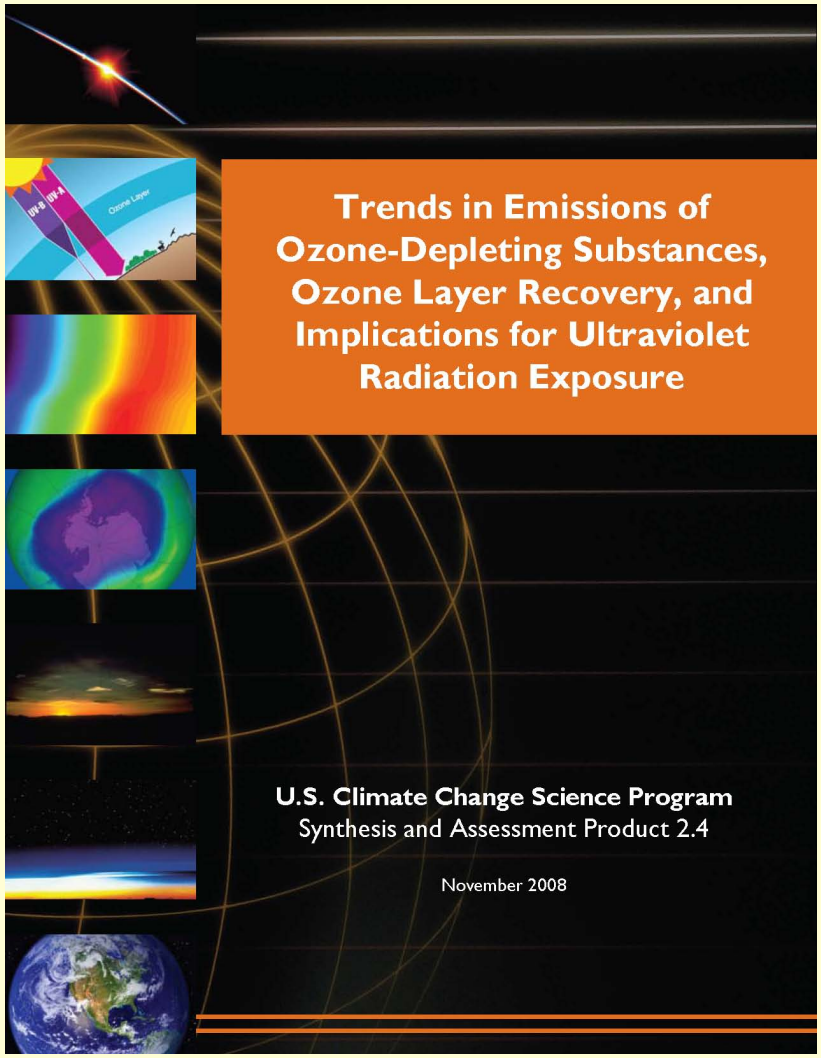
Future Ozone & Climate Research

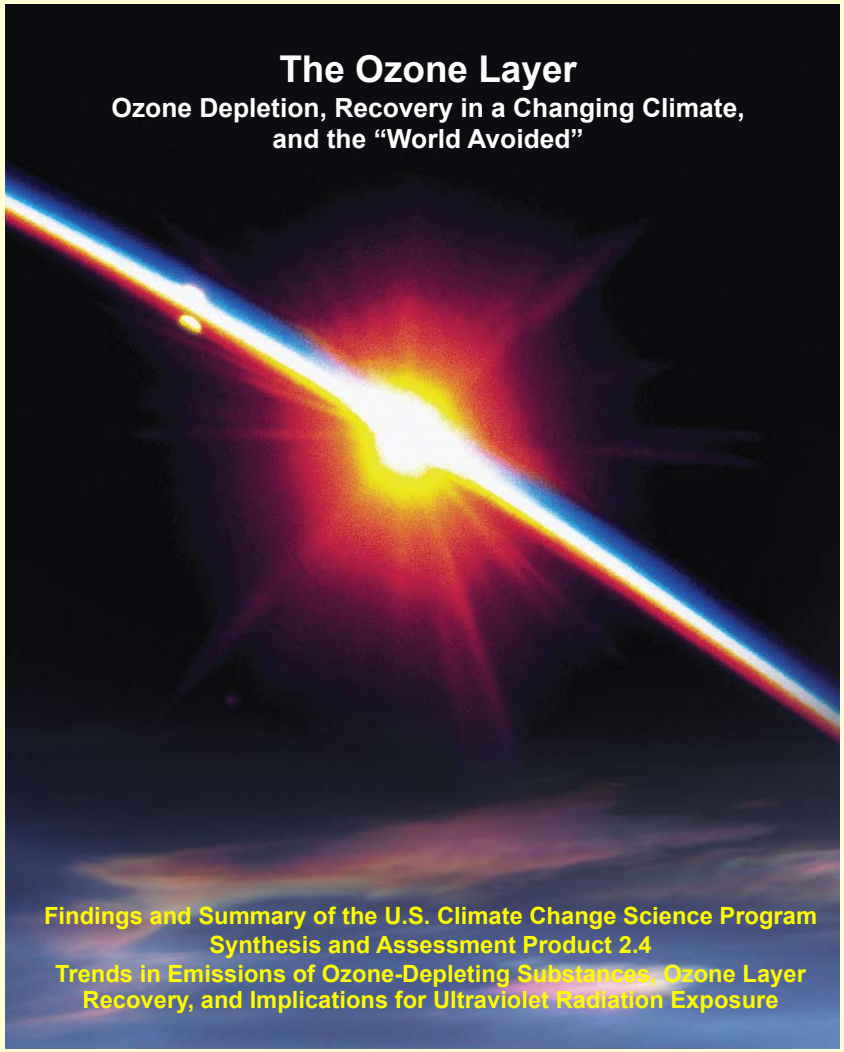
The continuation of integrated and coordinated observations is essential!

Atmospheric Measurements



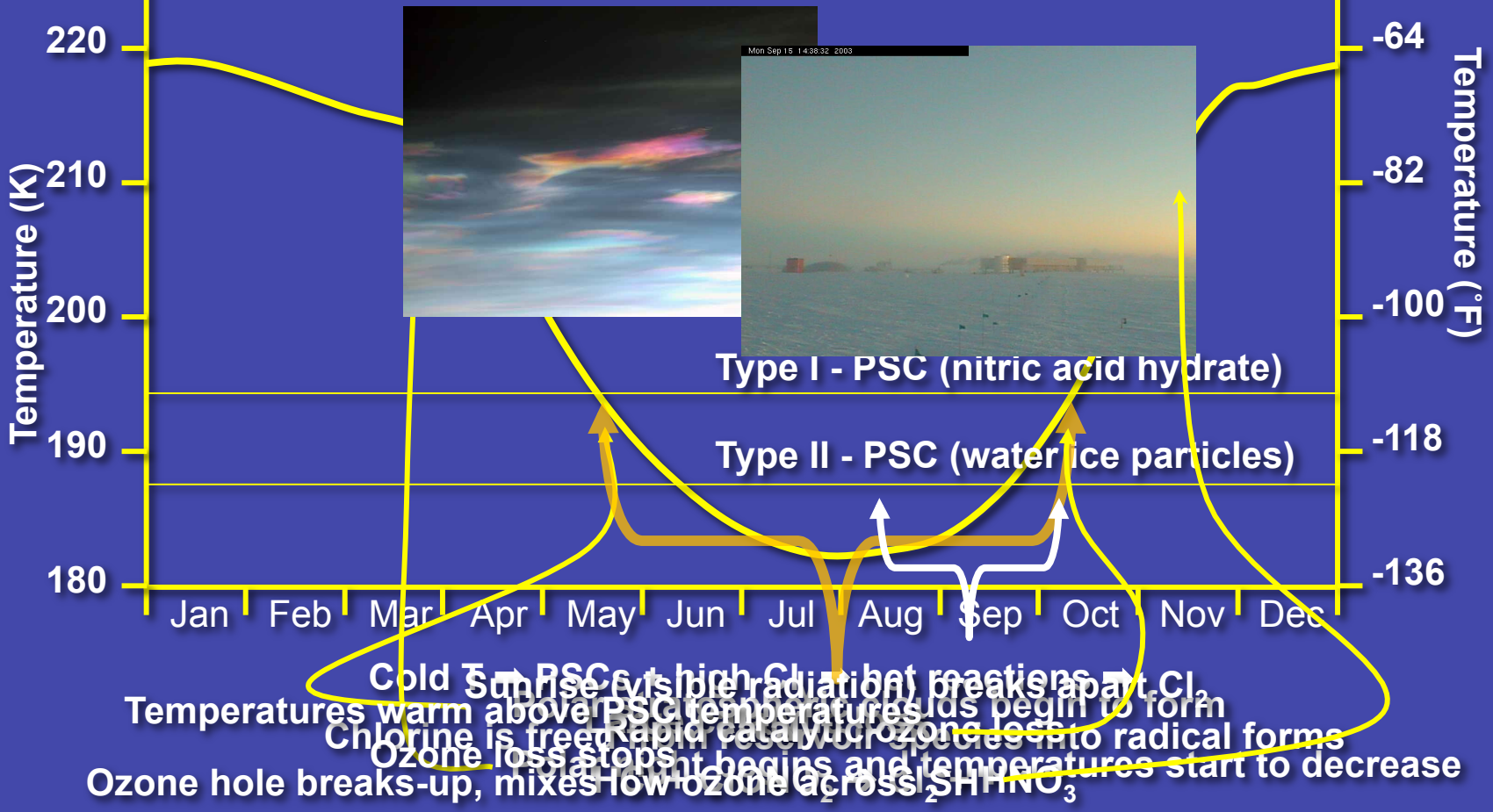
A United States-Specific Perspective of a Global Issue



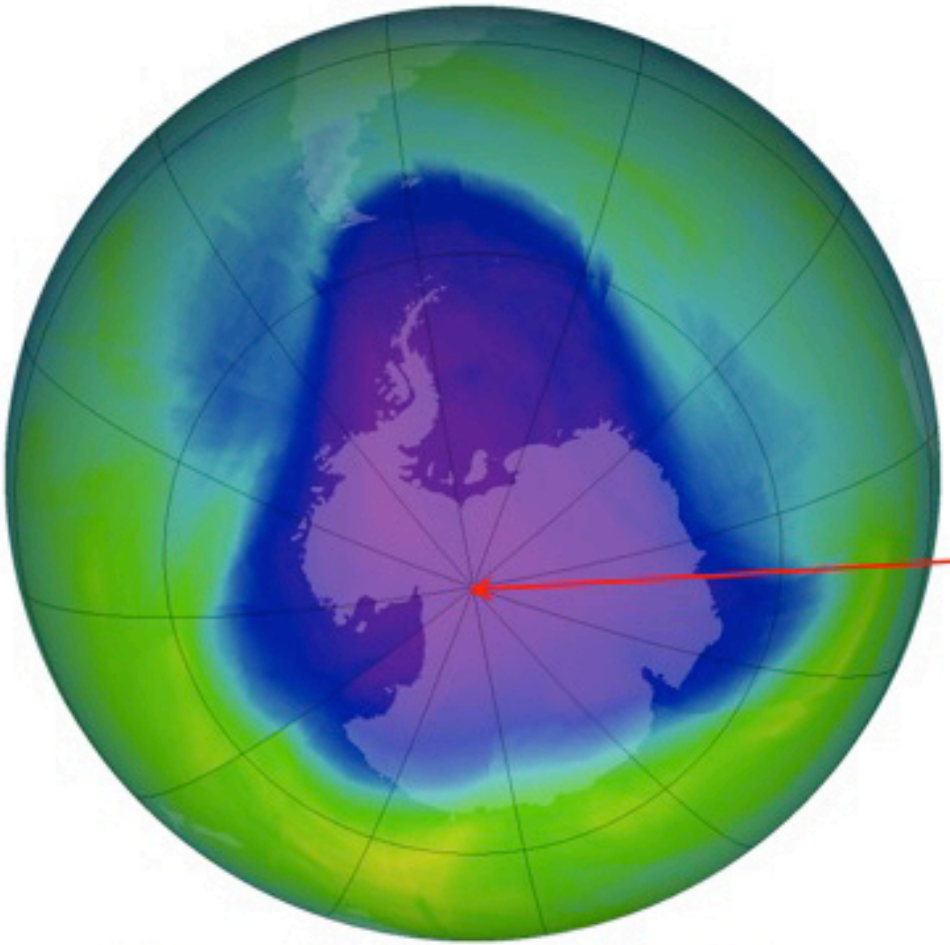


http://www.climatescience.gov/Library/sap/sap2-4/final-report/default.htm

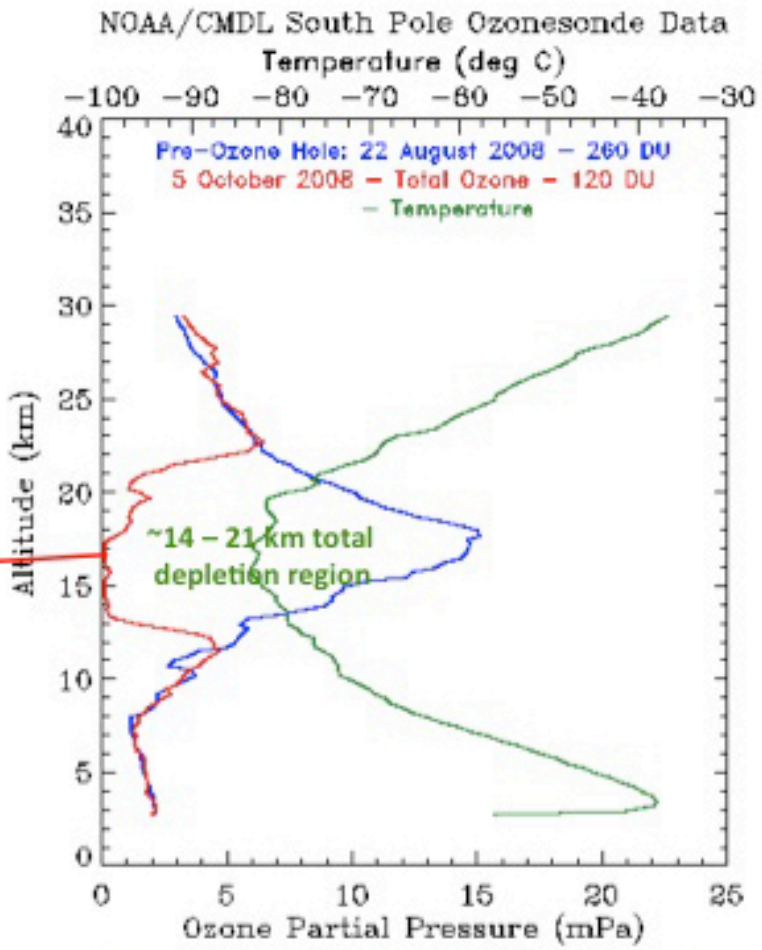
Antarctic Ozone Loss



2008 Antarctic Ozone Hole



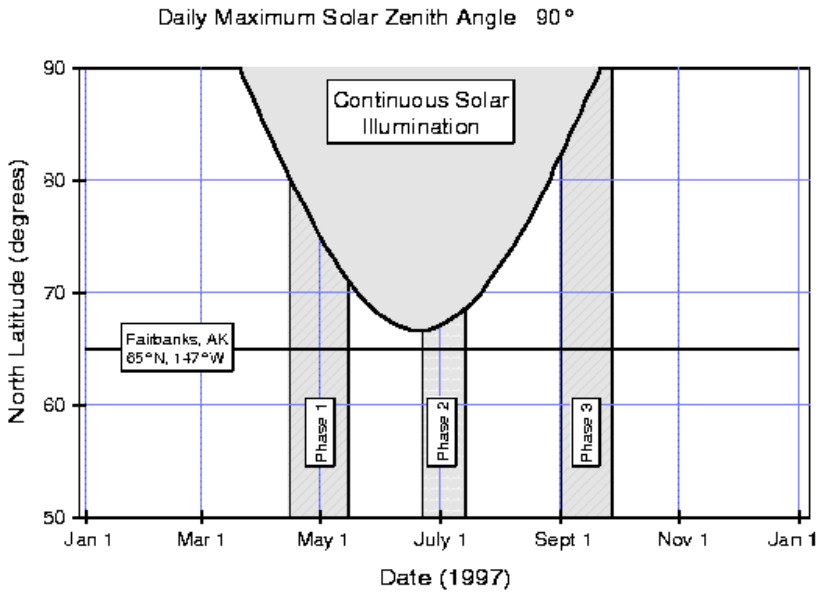
OMI Satellite Measurements – Oct. 5, 2008

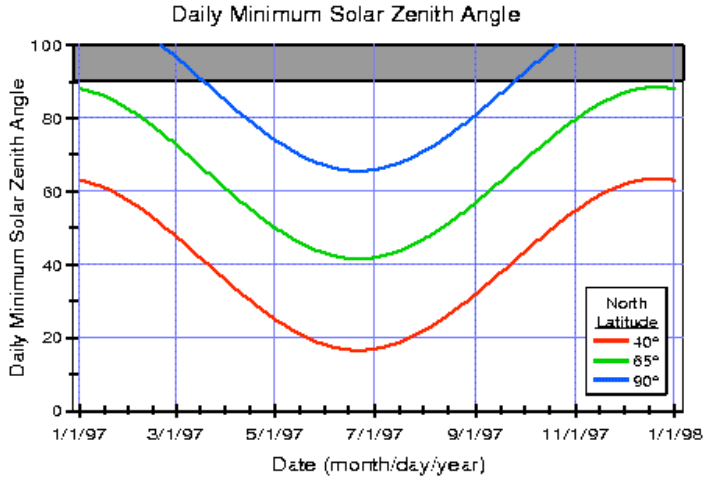


South Pole Balloon-borne Measurements
October 5, 2008

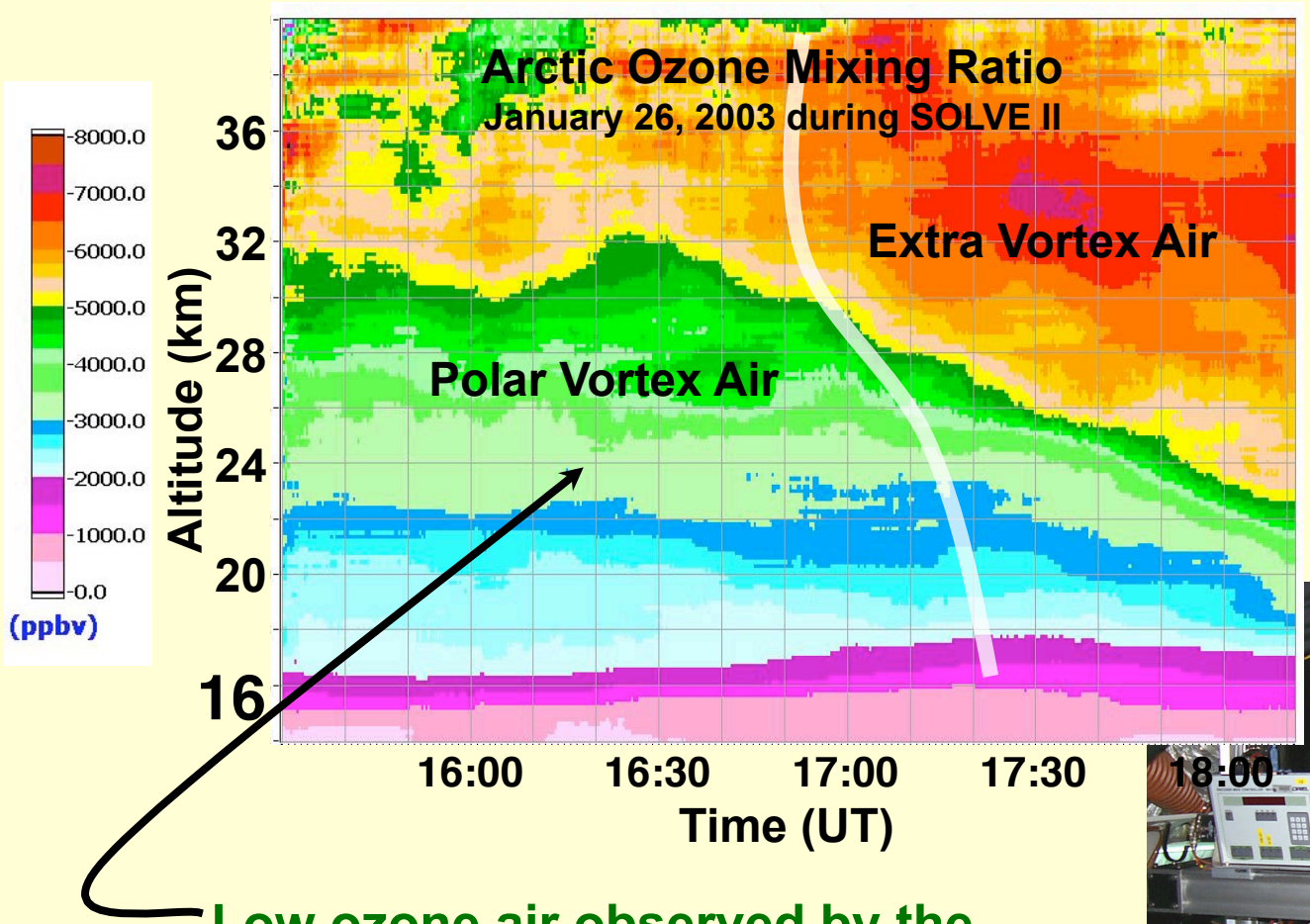
POLARIS Highlights

- A unique high latitude dataset on summer ozone changes in the lower stratosphere
- Improved understanding and prediction of photochemical partitioning and ozone loss rates
- Closure lacking in model / observation comparisons of summer ozone changes

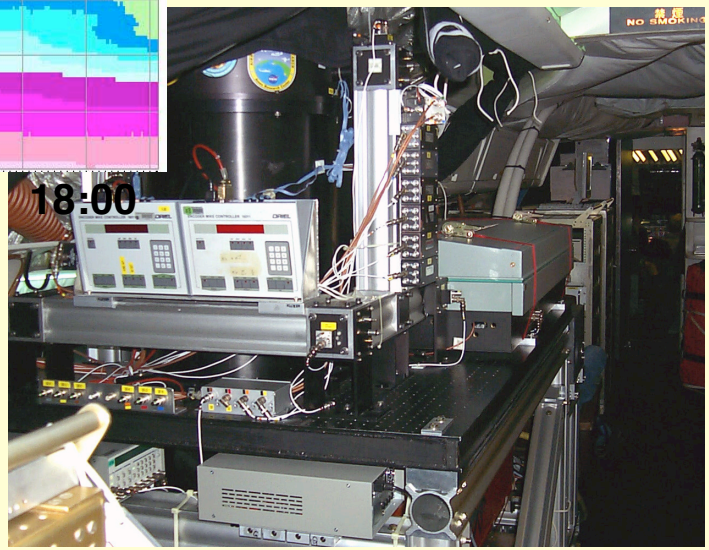




SOLVE-II:
LIDAR Observations of Ozone Loss



Airborne Raman Ozone, Temperature, and Aerosol Lidar (AROTAL) aboard the NASA DC-8 during SOLVE-II

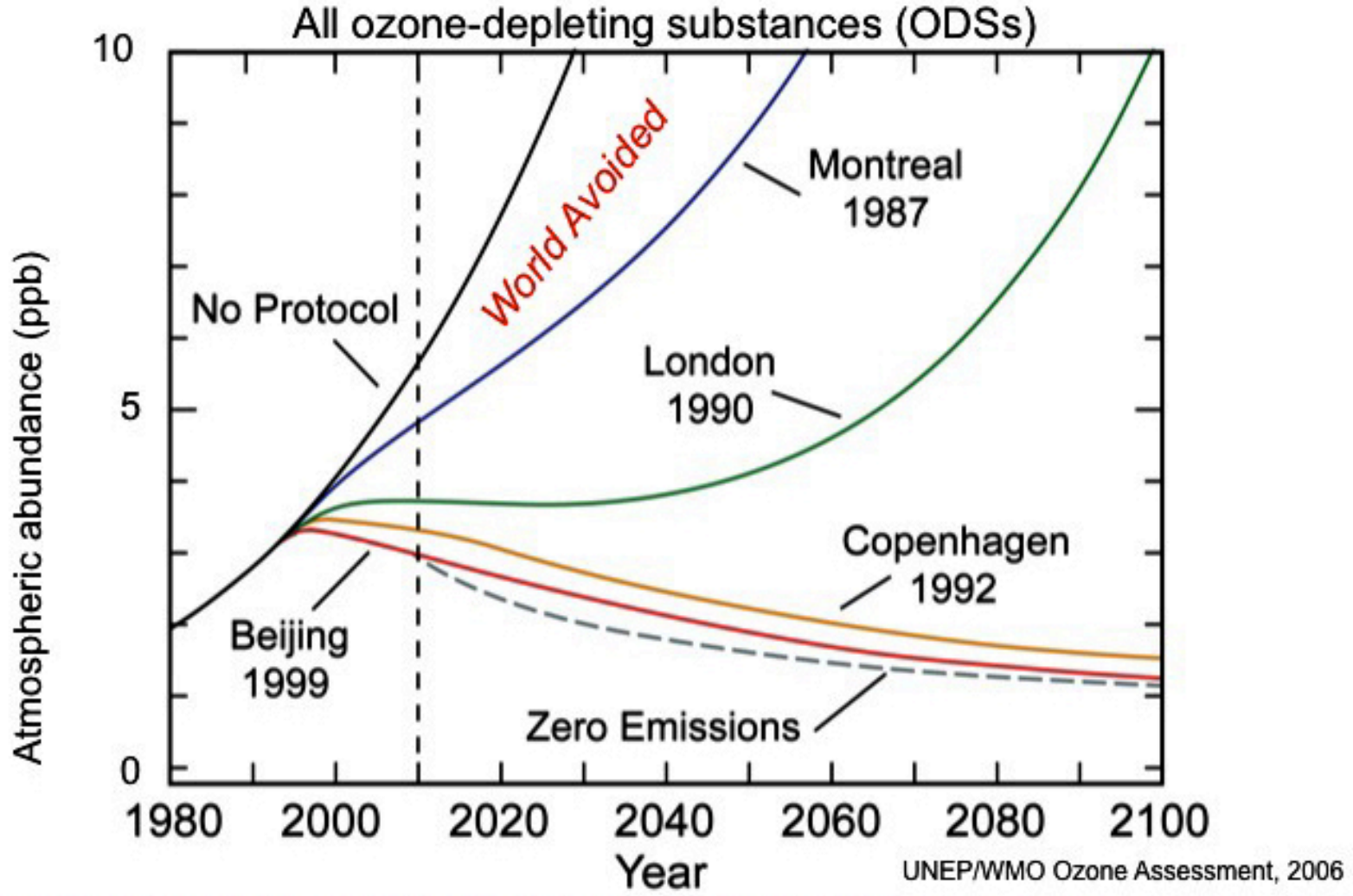


Low ozone air observed by the AROTAL LIDAR in late-January 2003 resulting from chlorine and bromine catalytic ozone loss reactions

Airborne Campaigns: A Critical Partnership Between Science and Operations!

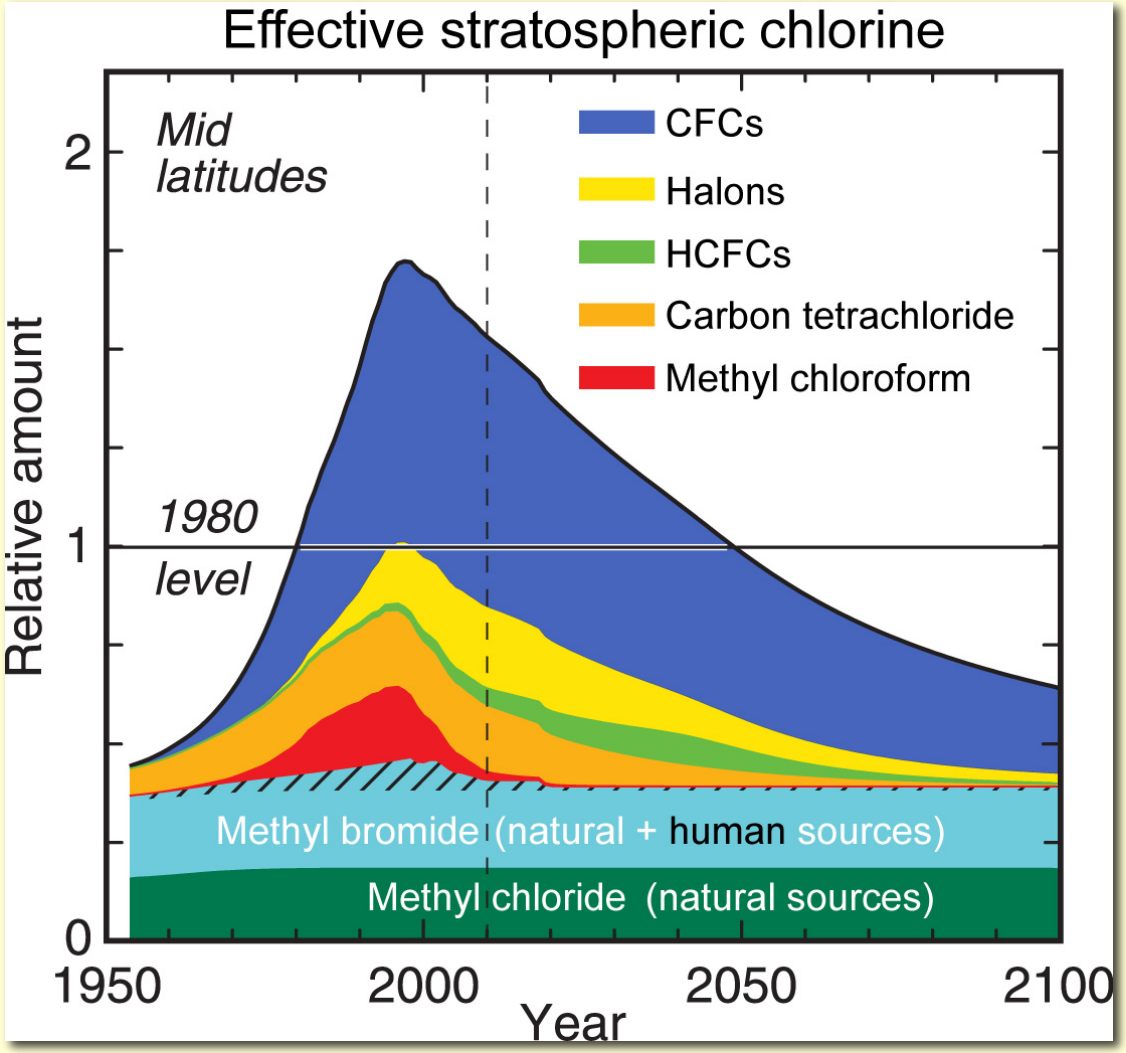
Polar Balloon Measurements

The Montreal Protocol and the World Avoided



The Montreal Protocol has successfully reduced global ODS production & consumption

The Success of the Montreal Protocol in Protecting Ozone

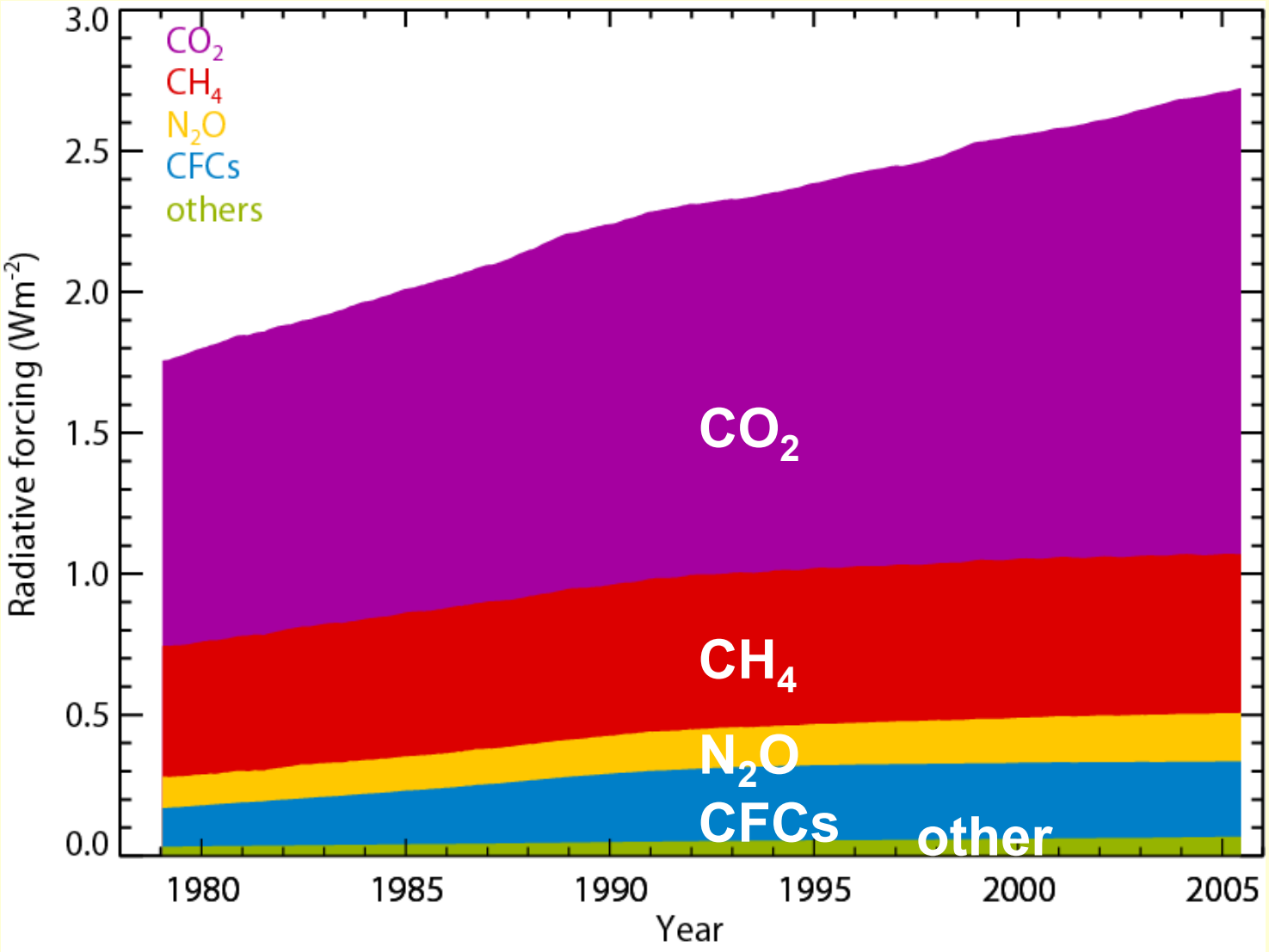


UNEP/WMO Ozone Assessment, 2006

The Montreal Protocol has slowed and reversed the accumulation of ozone depleting substances (ODSs) in the stratosphere.

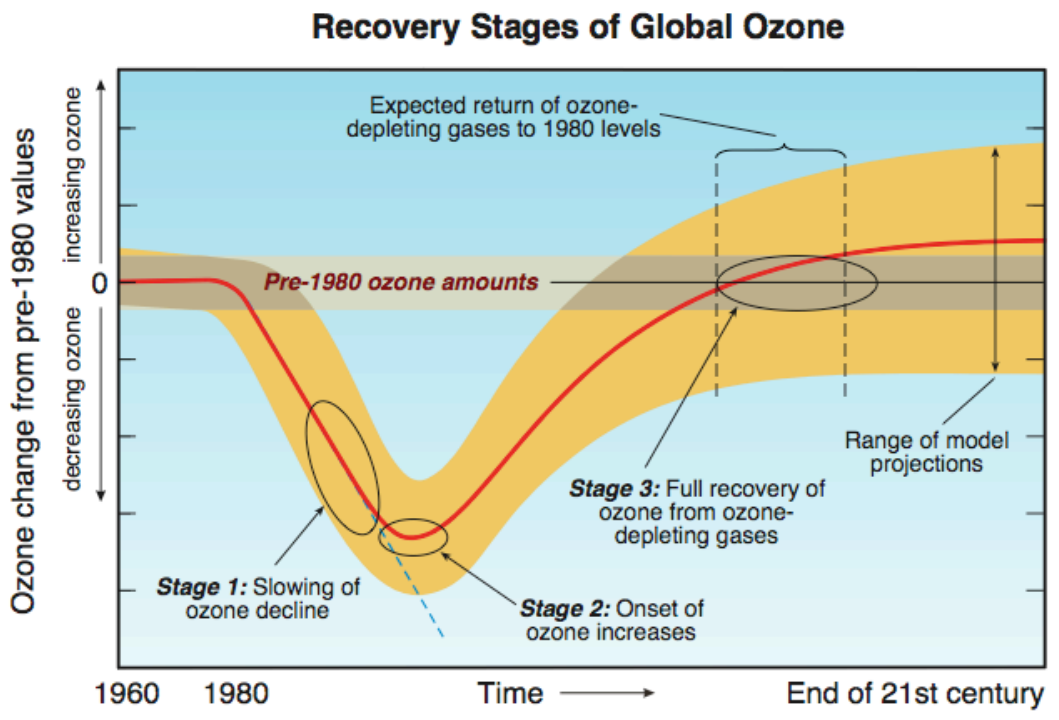
(Effective stratospheric chlorine is the weighted sum of chlorine and bromine gases in the stratosphere.)

Radiative Forcing from AGAGE Species and Carbon Dioxide



Return of Ozone to Pre-1980 Levels

- ODS are decreasing & the ozone layer is starting its recovery
- Climate change and ODSs will affect the future of ozone layer
- Decreases in ODS emissions already achieved by Montreal Protocol is the dominant factor in return to pre-1980 values



With continued compliance with the Montreal Protocol, the global ozone layer (60°S - 60°N) is expected to return to pre-1980 values around 2050